A LABORATORY GUIDE

FOR BEGINNERS

IN

CHEMICAL ANALYSIS.

FROM THE GERMAN OF DR. BIRNBAUM.

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NOTATION AND NOMENCLATURE.

The formulæ made use of in this work to describe compounds, are molecular formulæ; that is, they express the weight which, in the gaseous state, they have, referred to H_2, volume for volume. This is not the place to describe the methods by which the molecular volumes of volatile and non-volatile bodies have been determined. The molecule we believe to be composed of atoms having the smallest proportion, by weight, of the element which can enter into combination. The atoms unite with one another to form molecules, in which their affinities are mutually satisfied: the measure of affinity is different for different atoms: the elements differ in quantivalency or atomicity. The measure of the atom of hydrogen, H, is selected as a basis; it is univalent, and is, as it were, a point of departure for other atoms. The metalloids are called univalent, bivalent, trivalent, etc., according as an atom is able to unite with, or replace, one, two or three atoms of hydrogen. The quantivalency of the metals depends upon the number of hydrogen atoms which the metal-atom can replace.

Probably every atom has a fixed capacity for saturation—a fixed chemical value. But two or

more similar atoms may be so united that their value may be apparently lessened as truly through the union of these affinities as of other elements. For instance, C is quadrivalent; C — C at most (2. 4 —2) = sexivalent; or when both the C atoms are united through the two units of affinity (2. 4—4) = quadrivalent, etc. Similar relations are observed among some of the metals, some metals apparently possessing different quantivalencies in their compounds. These metals are divided into three classes.

1. Iron, manganese, chromium, cobalt, uranium, aluminium and nickel appear to be quadrivalent; but by union of the two atoms, *e. g.*, Fe—Fe or Fe = Fe, the double atom becomes hexivalent, so that the single atom of this element appears to be trivalent or bivalent. In notation in the case of the foregoing metals which have sesqui-oxides, we are accustomed to employ a double atom in this work: thus iron, in such compounds, will be written Ffe; the doubling of the initial letter indicates a double atom. (See page 49.)

Where it is necessary to use the old nomenclature, the compounds bear the names ferri-, mangani-, etc., salts. According to the above view, there are obtained for the protoxides and their compounds, formulæ which, being divisible by two, and for the sake of simplicity, contain only a single atom of iron, etc. Since, up to the present time, it has not been settled whether in the compounds of the protoxide series only two or more atoms are grouped together, the more familiar and simple

formulæ, *e. g.*, $FeCl_2$ are employed. These oxygen compounds are termed ferrous, manganous, etc., salts.

2. Platinum and tin are sometimes quadrivalent. In the binoxide compounds, platinic and stannic salts, the single atom is quadrivalent. In the protoxides, the platinous and stannous salts, the single atom is apparently bivalent, on account of such a grouping of two atoms that of each two affinities are satisfied (Sn=Sn). In this case the double atom may be indicated by a double letter, thus stannous chloride $SsnCl_4$, stannic chloride $SnCl_4$. But one may look upon the protoxide compounds as not saturated, since in the stannous salts only two of the four affinities of the single atom are satisfied, and the full quantivalency first appears in the stannic salts. Since there always is one metal atom in these oxides, and it is preferable to employ the simple and more familiar formulæ, stannous chloride may be written $SnCl_2$, and stannic chloride $SnCl_4$.

3. Mercury and copper are bivalent.

In the binoxides (mercuric and cupric compounds) there appear two affinities of the single atom. In the protoxides (mercurous and cuprous) there is a double atom, which, we believe, is produced by the grouping of single atoms. The double atom Hhg and Ccu is then bivalent. The single atom is plainly univalent in the protoxides. We express mercurous chloride by $HhgCl_2$, mercuric chloride by $HgCl_2$.

TABLE OF THE ATOMS

ACCORDING TO THEIR QUANTIVALENCE.

(In Round Numbers.)

METALLOIDS.

UNIVALENT.

H	=	1
Cl	=	35.5
Br	=	80
I	=	127
F	=	19

BIVALENT.

O	=	16
S	=	32
Sn	=	118

TRIVALENT.

N	=	14
P	=	31
B	=	11
As	=	75
Sb	=	122
Bi	=	208

QUADRIVALENT.

C	=	12
Si	=	28
Sn*	=	118

METALS.

UNIVALENT.

K	=	39.1
Na	=	23
NH_4	=	18
Ag	=	108
Cu	=	63.5
Hg	=	200

BIVALENT.

Ca	=	40
Ba	=	137
Sr	=	87.6
Mg	=	24
Zn	=	65
Cd	=	112
Pb	=	206
Cu*	=	63.5
Hg	=	200
Fe	=	56
Mn	=	55
Cr	=	53
Co	=	58.7
Ni	=	58.7
Pt	=	197.4

TRIVALENT.

Au	=	196
Fe	=	56
Mn	=	55
Cr	=	53
Co	=	58.7
Ni	=	58.7
Al	=	27.5

QUADRIVALENT.

Pt	=	197.4
Fe	=	56
Mn	=	55
Cr	=	53
Co	=	58.7
Ni	=	58.7
Al	=	27.5

SEXIVALENT.

Ffe	=	112
Mmn	=	110
Ccr	=	106
Coo	=	116.4
Nni	=	116.4
Aal	=	55

* In higher oxides.

METALLOIDS.

METALS.

COURSE OF ANALYSIS.

1. Preliminary Examination.

A substance proposed for analysis must first be examined with reference to its physical properties. The form (whether fluid or solid, crystalline or amorphous, homogeneous or mixed); the color, hardness, lustre and specific gravity must be noted. Then the body subjected to the action of chemical forces, and first of all to an elevated temperature.

1. *The substance is heated on platinum foil.*

a. It changes its color, becoming darker. If this phenomenon occurs, but speedily passes away, we may suspect the presence of Zn and Sn. If the darker color remains, Pb, Bi or some organic substances are present.

b. Observe whether the substance decrepitates, whether it evaporates or burns; whether, after continued heating, it becomes solid and remains so, or whether at a higher temperature it melts. (Thus sulphur is known, *e. g.*, by its burning away with formation of SO_2; iodine by the violet-vapors; observe whether a salt yields water; whether the salt freed from water is then infusible (*e. g.*, $Al_2S_3O_{12}$), or whether it fuses (*e. g.*, borax.)

2. *The substance is heated in a glass tube closed at one end.* By this means we may detect the volatile constituents of bodies separable by heat.

a. *Water* condenses in drops in the colder portions of the tube. Its reaction must be tested with litmus paper (alkaline—NH_3; acid—SO_2, HCl, etc.).

b. *Ammonium salts* are either volatile without decomposition and sublime (some directly from the solid state NH_4Cl, some after previously melting $((NH_4) SO_4)$, in the colder part of the tube; or they are decomposed. In the latter case there frequently remains, during the escape of NH_4, the hydrate of the acid, *e. g.*, $(NH_4)_3 PO_4$) or the salt is wholly broken up into gaseous products (NH_4NO_3.)

c. *Mercury compounds* yield, for the most part, when heated in the tube a deposit of metallic mercury; only $HgCl_2$, $HgBr_2$, HgI_2 are volatile without decomposition.

d. *Arsenic compounds* often give a sublimate of As_2O_3 or a metallic mirror. *Sulphur* and its compounds, with many metals, yield a yellow sublimate of sulphur, which melts to red drops.

3 The substance is heated with Na_2CO_3 and KNO_3, *oxidizing fusion.* By this means especially Mn and Cr may be detected, by the green or yellow enamel.

4. The substance is heated on charcoal before the blowpipe, *reducing flame.*

a. On heating the body alone on charcoal, the observation before mentioned may, in part, be repeated. Arsenic compounds yield a garlic odor. Metallic sulphides yield sulphurous acid, etc. If the substance melts and is absorbed by the charcoal we suspect salts of the alkalis. If the substance leaves behind an infusible white residue, there is

ground to infer the presence of Ba, Si, Ca, Mg, Al_2 and Zn. The residue is then moistened with some CoN_2O_6 and again ignited. If it thereby becomes blue it contains Al_2; if green, it is Zn; if it becomes flesh color, it contains Mg. If the body deflagrates on heating it on charcoal, it contains either a chlorate or a nitrate. We then test the reaction of the residue, if it be alkaline (nitrates) or neutral (chlorates).

b. Some of the original substance is mixed with Na_2CO_3 and KCy, and the mixture is heated before the blowpipe on charcoal. Arsenic compounds evolve by this means also the odor of garlic. Sulphur compounds yields a sulphur slag (hepar). Many metals are reduced.

a. Metal without incrustation—infusible, Ni, Co, Fe, (Pt, Mo, Wo); fusible, Cu, Ag, Au, Sn.

b. Metallic globule with incrustation—Sb, brittle, incr. white and volatile; Bi, brittle, incr. brownish yellow. Pb, malleable-incr., bright yellow.

c. Incrustation without metallic globule: Zn white, yellow when hot, unchanged by heating. Cd dark brown.

5. The substance is heated on platinum wire, in a non-luminous flame. *The flame becomes colored* by K violet, by Na yellow, by Si dark red, by Sr crimson, by Ca reddish yellow, by Ba greenish yellow, by Cu azure, by B_2O_3 green.

6. The substance is fused on platinum, on which is a clear bead of mic. salt ($NaNH_4HPO_4$) or borax ($Na_2Bo_4O_7$). The beads assume colors characteristic of the metals.

The flame which is now blown upon the bead must be a luminous one. In such a flame the outer part oxidizes the substance, the inner reduces; h stands for hot, c for cold.

	Oxidizing flame.	*Reducing flame.*
Cr..........	green	green
Fe ....red (h)	colorless (c)	green
Co	blue	blue
Cu .... green (h)	blue (c)	brown opaque
Mn.........	amethyst	colorless
Ni (borax).. red (h)	yellow (c)	gray (metal) especially on addition of tin.

SiO_2 gives in the mic. salt bead a skeleton.
Ba, Ca, Mg, added in large amount give a milk white bead.

The preliminary testing for acids has been described under metalloids. This preliminary examination throws light on the composition of simple salts. The foregoing reactions serve to confirm the presence of substances detected in the wet way. Mixtures are to be studied in the wet way.

2. Directions for Dissolving the Substances to be Tested.

a. If the substance is metallic, heat it with conc. HNO_3. An insoluble white residue consists of Sb_2O_4 or SnO_2. This is dissolved in yellow ammonic sulphide. Sb_2S_3 and SnS_2 are precipitated from the solution by HCl, and tested for Sb and Sn as previously directed.

b. The substance is not a metal.

a. It is heated with water and watched to see if it dissolves. If there is a considerable amount

dissolved the watery solution must be examined by itself. If traces only of the substance are dissolved, it may be treated as if it were insoluble in water.

b. One portion of the original substance, insoluble in water, is treated with moderately dilute hot HCl, and another in like manner with HNO_3. The acid which proves the better solvent is employed in dissolving the part insoluble in water.

c. That which proves insoluble in HCl or HNO_3 is finally heated with aqua regia. In this are insoluble: AgCl, $BaSO_4$, $SiSO_4$, $PbSO_4$, SiO_2, CaF_2 ignited, Al_2O_3, Cr_2O_3 SnO_2 and C. The residue is digested with NH_5O. In this AgCl is soluble (precipitated again on adding HNO_3). With portion not soluble in NH_5O the following investigations are made:

1. One portion is ignited with Na_2CO_3 and KCy on charcoal. Hepar shows the presence of sulphate. Metallic globules indicate tin or lead.

2. A second portion is brought into a phosphorus bead. SiO_2 gives a skeleton; Cr_2 colors it green.

3. Upon a third portion is poured conc. H_2SO_4. If CaF_2 is present, HF is thereby evolved.

According to the result of these researches, break up the substance either by fusion with Na_2CO_3 (1 and 3), or with $KHSO_4$ (ignited oxides). The fused mass is treated with water, and the residue insoluble in water is dissolved in HCl.

Almost all compounds not soluble in aqua regia may be decomposed in the following way: The

insoluble substance is mixed with twice its weight of Na_2CO_3 and 14 times its bulk of a mixture of one part powdered charcoal and 6 parts KNO_3. The mixture is kindled in a porcelain capsule by a glowing splinter, the cold mass extracted with water, and what remains may be dissolved in acids.

3. Detection of Metals in Solution.

Solutions prepared according to the foregoing directions are made slightly acid; aqueous solutions are decomposed with a little HCl; the solutions in acids are freed from excess of acid by evaporation. Solutions must not be too dilute, neither must they contain too much acid (HNO_3 least of all). If a precipitate forms on the addition of HCl, it is disregarded and the solution is saturated with gaseous H_2S. The precipitate collected on a filter and washed with a dilute solution of H_2S. (See pages 68 and 77.) The filtrate is treated with NH_4Cl saturated with NH_5O and NH_5S is added in slight excess. The resulting precipitate is collected on a filter, washed with water containing a little NH_5S, and then treated as directed on page 57. The filtrate is acidified with HCl, heated to expel all H_2S, filtered from the separated sulphur, and the solution tested for the metals of the alkaline earths and alkalis, as directed on page 44.

It is not advisable to mix the aqueous and acid solutions of the substance. The aqueous solution contains the alkali compounds; in the acid solutions it is seldom necessary to search for these, but the acid solutions may contain the phosphates of the

metals of the alkaline earths, etc., which are rarely found in aqueous solution; the examination of the NH_5S precipitate from an aqueous solution is much more simple than that thrown down from an acid solution.

4. Detection of the Acids.

We have already given directions for this part of the analysis (page 34). This course, however, must be modified when certain metals are present. The solution which results from heating the substance with Na_2CO_3 may contain As, Sn, Al, Cr, Zn.

In order to recognize these bodies, add to a part of the filtered solution dilute H_2SO, to slight acid reaction, test with H_2S for As and Sn, filter and test the filtrate with NH_5O and NH_5S for Al_2, Cr_2 and Zn. If any of these metals have been found, next test a part of the original solution with $BaCl_2$ for sulphates; acidify the remainder slightly with H_2SO_4, precipitate by H_2S, NH_5O and NH_5S, then add a little H_2SO_4 heat to expel H_2S, filter from the separated sulphur, and examine for the acids as directed on page 34.

METALLOIDS.

I. UNIVALENT METALLOIDS.

1. Hydrogen.

Atom $H = 1$; Molecule $H_2 = 2$.
Vapor density $= 0.06926$.

A colorless, odorless, inflammable gas, which by combustion in oxygen forms water.

2. Chlorine.

At. $Cl = 35.5$; Mol. $Cl_2 = 71$.
Vapor density $= 2.45$.*

Greenish yellow gas of peculiar odor. Water absorbs at $+ 8^\circ$ C. four times its volume of this gas. In the light, chlorine-water is decomposed with evolution of oxygen. Free chlorine colors starch-paste, containing potassic iodide, blue (separation of I_2); hydrosulphuric acid (H_2S) is decomposed with precipitation of sulphur; from ammonia, chlorine

* The density of a vapor referred to air as unity may be converted into that which it has compared with hydrogen, by dividing by .06926 the specific gravity of hydrogen referred to air as unity.—*Watts.*

liberates nitrogen. In the presence of water it acts as an oxidizing agent, throwing down, for example, from a neutral solution of lead ($PbC_4H_6O_4$) a bright brown precipitate of $PbCl_2$ and PbO_2, and converts salts of dyad iron into those of hexad iron (potassic sulphocyanate). Organic coloring matters (indigo) are destroyed by chlorine.

Hydrochloric acid (HCl), *Muriatic acid*, is a colorless gas of a pungent, suffocating odor, which fumes in the air, and with ammonia forms a white cloud of ammonic chloride. Water absorbs this gas in large quantity; and this aqueous solution is a powerful solvent for bodies insoluble in water. It dissolves metals with evolution of H_2 (Zn), or by the aid of free oxygen (Cu); by dissolving basic metallic oxides (CaO, Fe_2O_3) in hydrochloric acid, metallic chlorides and water are formed; the higher oxides (MnO_2) and the metallic acids (CrO_3) yield, on heating with HCl, besides metallic chlorides and water, free chlorine; from salts hydrochloric acid displaces the other acids wholly ($CaCO_3$, $CaSiO_3$), or in part ($Ca_3P_2O_8$).

To detect hydrochloric acid, in the presence of free chlorine, the liquid is shaken with mercury, filtered from the insoluble residue of mercurous chloride (Hg_2Cl_2) and tested for hydrochloric acid. Pure hydrochloric acid reddens litmus paper, but does not bleach it.

The metallic chlorides derived from hydrochloric acid, which are formed when the metal-atom, according to its quantivalence, replaces the hydrogen of the hydrochloric acid, are almost all soluble in

water; Cu_2Cl_2, $PbCl_2$ are soluble with difficulty; $AgCl$, Hg_2Cl_2, $AuCl$, $PtCl_2$ and the violet Cr_2Cl_6, are insoluble.

Hydrochloric acid and soluble metallic chlorides give with *argentic nitrate* ($AgNO_3$) a white, flocculent precipitate ($AgCl$) which blackens in the light, dissolves readily in ammonic hydrate, but is insoluble in nitric acid. *Mercurous nitrate* ($Hg_2N_2O_6$) produces with Hydrochloric acid, or metallic chlorides, a white precipitate (Hg_2Cl_2) which is easily soluble in chlorine water (forming $HgCl_2$), is not affected by dilute acids, but when ammonic hydrate is poured over it, turns black ($Hg_2Cl_2 + 2NH_5O = Hg_2H_2NCl + NH_4Cl + 2H_2O$). With *plumbic acetate* ($PbC_4H_6O_4$) they give a white crystalline precipitate ($PbCl_2$) which is soluble in much water.

All the metallic chlorides, except the chlorine compounds of Ag, Hg, Pb and Sn, treated with hot concentrated sulphuric acid, evolve hydrochloric acid gas with the formation of sulphates; with manganic peroxide and sulphuric acid they yield sulphates and free chlorine; with dry potassic chromate (K_2CrO_4) and concentrated sulphuric acid they yield sulphates and chromoxychloride (CrO_2Cl_2), brownish-red vapors, which condense to blood-red drops, and form with ammonic hydrate a yellow solution (composed of NH_4Cl and $(NH_4)_2CrO_4$).

Of the five compounds of chlorine and oxygen the following, only, are mentioned here.

1. *Perchloric acid* $HClO_4$ (anhydride Cl_2O_7) crystallized, is very stable. All its salts are soluble in water, the potash salt is the least so. Perchlorates

are decomposed with deflagration upon charcoal before the blowpipe. Perchloric acid is liberated from its salts by sulphuric acid, but is not thereby decomposed. The aqueous solutions of perchlorates do not bleach vegetable colors, even upon the addition of an acid.

2. *Chloric acid* $HClO_3$ (anhydride Cl_2O_5) readily yields by heating in water, chlorine and oxygen. The chlorates without exception are soluble in water. Before the blowpipe, on charcoal, they deflagrate violently and leave behind a neutral residue of metallic chloride, soluble in water. With HCl the chlorates evolve chlorine with formation of water and metallic chloride. When concentrated sulphuric acid is poured upon them, the chlorates first become colored brown, and then form sulphate and perchloric acid, while there is liberated chloric tetroxide (Cl_2O_4), a greenish-yellow gas, which is easily decomposed with explosion into Cl_2 and $2\ O_2$. (Only a small quantity of the chlorates should be employed.) An aqueous solution of the salts bleaches only upon the addition of an acid.

3. *Hypochlorous acid* HClO (anhydride Cl_2O), is stable only in the dark. The hypochlorites are all soluble in water; they are generally mixed with metallic chlorides, constituting bleaching salts. By heating they yield metallic chlorides and chlorates. With acids pure hypochlorites evolve hypochlorous acid (with HCl they give off chlorine); with all acids bleaching salts yield chlorine. Aqueous solutions bleach, even by themselves; more powerfully upon the addition of an acid. With ***argentic nitrate***

and mercurous nitrate the hypochlorites yield the corresponding metallic chlorides, with evolution of oxygen; with lead salts they yield, in the cold, $PbCl_2$ and O_2; by heating, brown PbO_2 and Cl_2; with manganese salts they yield brown MnO_2 and Cl_2; with ammonic hydrate they evolve nitrogen.

*TABLE.**

	$AgNO_3$	$PbC_4H_6O_4$	$MnCl_2$	HCl	H_2SO_4	NH_5O	Indigo.	On charcoal, before the blowpipe.
Cl_2 ...	$AgCl(AgClO_3)$	$PbCl_2+PbO_2$	—	—	—	N_2	Decolorizes	—
KCl ..	AgCl	$PbCl_2$	—	—	HCl	—	—	—
KClO.	AgCl(O)	$PbCl_2(PbO_2)$	MnO_2	Cl_2	$Cl_2O(Cl_2)$	N_2	Decolorizes	—
$KClO_3$	—	—	—	Cl_2	Cl_2O_4	—	Decolorizes upon addition of HCl	Deflagrates
$KClO_4$	—	—	—	—	$HClO_4$	—	—	Deflagrates

* While the beginner, by examples for practice, learns to distinguish from each other the acids described above, he will find time for the quantitative estimation of the chlorine, for instance, in common salt.

3. Bromine.

At. Br. = 80; Mol. Br_2 = 160.
Vapor density = 5.5.

Bromine is a dark brown, almost black, liquid (of 3.18 specific gravity), which boils at 63° C. and solidifies at —7.3° C. Even at ordinary temperatures it is very volatile, giving off a brown vapor which has a characteristic disagreeable odor. In water it is only slightly soluble, but in alcohol, ether and carbonic disulphide it dissolves readily to a brown color.

Free bromine, hydrobromic acid and metallic bromides behave exactly like the corresponding chlorine compounds, with the following exceptions:

1. *Free bromine* dissolves in carbonic disulphide to a brown color; starch paste is colored bright red by it.

2. *Metallic bromides* yield, with concentrated sulphuric acid, besides HBr, free bromine and sulphurous acid. With concentrated sulphuric acid and potassic chromate they yield free bromine. When chlorine water is poured upon them, bromine is separated from them; by shaking with CS_2, the free bromine can be extracted from the liquid; the CS_2 is thereby colored brown. Argentic bromide is less easily soluble than argentic chloride in NH_5O.

The only compound of bromine with oxygen to be mentioned here, is *bromic acid* ($HBrO_3$) (anhydride Br_2O_5). In its behavior it closely resembles chloric acid. The bromates resemble the chlorates, with the following exceptions: With concentrated sulphuric acid, bromates, without explosion, yield Br_2

and O_2; on charcoal, before the blowpipe, deflagrate, leaving a residue of metallic bromides. With $AgNO_3$ they give a precipitate ($AgBrO_3$) which is readily dissolved in NH_5O, but is difficultly soluble in HNO_3; $AgBrO_3$, differs from argentic chloride ($AgCl$) in this respect, that it yields Br_2 when concentrated sulphuric acid is poured upon it.

The bromates and the metallic bromides, when together, are easily distinguished, for such a mixture gives, with dilute acids, free Br_2, while neither of the constituents, when alone, will show this reaction.

Discrimination between Metallic Chlorides and Bromides.

1. A part of the substance is tested, with Cl_2 and CS_2, for Bromine.
2. Another portion of the dry substance is mixed with dry K_2CrO_4, and the mixture is heated with concentrated sulphuric acid. If a metallic chloride is present, CrO_2Cl_2 (page 3) is formed.

4. Iodine.

At. I. = 127; Mol. I_2 = 254.
Vapor density = 8.8.

At ordinary temperatures iodine is a gray solid of metallic lustre; specific gravity, 4.9; melting point, 107° C.; boiling point, 180° C. It is volatile even at ordinary temperatures, diffusing violet vapors, of characteristic odor, which easily condense to foliated crystals. Iodine is slightly soluble in water, dissolves readily in alcohol, ether, or an

aqueous solution of potassic iodide, giving a brown color; in carbonic disulphide gives a violet color.

Free iodine in its deportment closely resembles chlorine and bromine. From these iodine is plainly distinguished by the violet color which it imparts to carbonic disulphide, and by the blue color which it gives to starch paste. Blue iodide of starch is decolorized by heat, but in the presence of substances which can set iodine free from its combinations, remains colored (for example, KHO gives KI and KIO_3, H_2SO_3 gives H_2SO_4 and HI, Cl_2 gives ICl_5, etc.).

Hydriodic acid and metallic iodides differ from the corresponding chlorine and bromine compounds, in the following particulars: In water there are insoluble, besides those iodine compounds corresponding to the insoluble metallic chlorides and bromides, also mercuric iodide HgI_2 and palladious iodide PdI_2. Yellow argentic iodide is insoluble in HNO_3 and in NH_5O, when quite pure it is unaffected by light. With cupric salts ($CuSO_4$) metallic iodides give cuprous iodide (Cu_2I_2) (most readily upon the addition of H_2SO_3, by which the free I_2 is removed). With concentrated H_2SO_4 the metallic iodides yield free iodine, sulphurous acid and sulphates. With concentrated H_2SO_4 and MnO_2, or K_2CrO_4, also free iodine, I_2. Nitrous acid (potassic nitrite KNO_2, in acid solution) sets iodine free from metallic iodides (formation of NO). When the metallic iodides are shaken with a little chlorine water they yield free I_2, recognized by means of CS_2 or starch.

Iodic acid HIO_3 (anhydride I_2O_5) crystallizes.

The alkaline iodates are soluble in water, all others are insoluble. Argentic iodate is a white flocculent precipitate, which separates when a solution of an iodate is decomposed by argentic nitrate; it is soluble in NH_5O, very difficultly soluble in HNO_3. Only HIO_3 is set free from the iodates by sulphuric acid, but this is not decomposed. If metallic zinc is added to a solution of an iodate in dilute H_2SO_4, there are formed, by means of the nascent hydrogen, water and hydriodic acid, and this yields free iodine, with simultaneous formation of iodic acid. KI produces in a solution of an iodate, acidified with H_2SO_4, a separation of I_2.

On this account an iodate is converted into a metallic iodide to be tested; it is necessary merely to acidify the solution with sulphuric acid. If both compounds are present, iodine is separated; neither alone gives this reaction.

TABLE.

	Cl_2	Cl_2+CS_2	Cl_2 and Starch.	H_2SO_4	H_2SO_4 $+K_2CrO_4$	N_2O_3
KCl ..	—	—	—	HCl	CrO_2Cl_2	—
KBr ..	Br_2	Brown	Red	$HBr(Br_2)$	Br_2	—
KI ...	I_2	Violet	Blue	I_2	I_2	I_2

Detection of Metallic Chlorides, Iodides and Bromides, in the presence of each other.

The presence of these bodies is shown by $AgNO_3$. If in an aqueous solution of a body there is produced, by $AgNO_3$, a precipitate insoluble in HNO_3, the metallic chlorides, bromides and iodides are identified in the following manner:

1. A part of the aqueous (neutral or slightly acid) solution is shaken with CS_2 and a little Cl_2. CS_2 violet: iodine — brown: bromine. If a metallic iodide has been detected, an excess of Cl_2 is added until the violet color of the CS_2 disappears. If the CS_2 is then brown, there is a metallic bromide present with the iodide; if the CS_2 is colorless, the absence of a metallic bromide is shown.

2. If a metallic iodide has been detected, test for a metallic chloride by precipitating the aqueous solution with $AgNO_3$, treating the precipitate with NH_5O, filtering, and acidifying the filtrate with HNO_3. Any AgCl previously dissolved by NH_5O is now precipitated.

3. A metallic chloride can be detected in the presence of a metallic bromide only when the chlorine is driven off as CrO_2Cl_2.

Insoluble compounds are fused with Na_2CO_3, the fused mass is dissolved in water, the filtered solution is neutralized by HNO_3 and tested as before described. Instead of fluxing with Na_2CO_3, it can be heated for a long time in a concentrated solution of this salt, filtered, and the filtrate then treated

as the aqueous extract of the fused mass above mentioned.

5. FLUORINE.

At. $F = 19$; Mol. $F_2 = 38$.

Fluorine is the only metalloid which we have been unable to isolate.

Hydrofluoric acid HF, is a colorless corrosive gas, powerfully attacking the respiratory organs; easily condensed to a liquid; absorbed by water in large quantities. Hydrofluoric acid differs from all other acids in that it dissolves silicic acid with the formation of silicic fluoride (SiF_4) and hydrofluosilicic acid (H_2SiF_6).

Hydrofluoric acid dissolves the silicic acid of silicates; it also etches glass. Of the metallic fluorides those of the alkaline metals are soluble in water, and possess an alkaline reaction. Of the compounds of fluorine with the other metals the following, only, are soluble in water: AgF, HgF_2, Fe_2F_6, Al_2F_6, SnF_2. The metallic fluorides insoluble in water dissolve in hydrofluoric acid, forming crystallizable double salts.

With concentrated sulphuric acid fluorine compounds give off hydrofluoric acid, which can be recognized by its etching glass. (See, also, silicon and boron.)

II. BIVALENT METALLOIDS.

6. Oxygen.

At. O = 16; Mol. O_2 = 32.
Vapor density, 1.106.*

Oxygen is a colorless, odorless permanent gas; a glowing splinter of wood when plunged into it bursts into flame. Oxygen, in combination, is detected by ignition in a stream of hydrogen, or mixed with carbon. The water produced in the first instance, or the carbonic oxide or acid in the latter, prove the presence of oxygen.

7. Sulphur.

At. S.=32; Mol. S_6=192 (at 500° C.) S_2=64 (above 800° C.)
Vapor density at 500° C.=6.634; above 800° C.=2.216.

Sulphur is a yellow solid which can exist in three forms. In nature, or from solutions, it crystallizes in elongated octahedrons; by slow cooling from the melted state, in oblique prisms; by sudden cooling from a temperature above 250° C. it is obtained as an amorphous mass. The specific gravities of these modifications differ from each other, being respectively 2.05, 1.96. 1.91.

Sulphur melts at 110° C.; becomes viscid at 160° C.; at 250° C. it is a limpid liquid; at 420° C. it boils.

Heated with access of air, sulphur takes fire at 270° C. In water, S_2 is insoluble; CS_2, sulphur chloride and volatile oils dissolve it. Sulphur is

* 1.1056.—*Watts's Dict.*, iv., 288.

easily recognized by its inflammability, and by the odor of the sulphurous acid formed from its combustion.

Hydrosulphuric acid H_2S, is a colorless gas of a characteristic disagreeable odor. The gas burns with a blue flame, yielding water and sulphurous acid. At ordinary temperatures water absorbs two or three times its volume of this gas. Exposed to the air, this aqueous solution becomes cloudy from separation of sulphur. Hydrosulphuric acid gas acts as a reducing agent, depriving the higher compounds of chlorine, oxygen, etc., of chlorine, oxygen, etc., with formation of hydrochloric acid, water, etc., and separation of sulphur (e. g., Fe_2Cl_6, HNO_3, H_2CrO_4).

The gas decomposes all metallic oxides with the formation of metallic sulphides, and water. The metals are divided into three great classes, according as their sulphides are soluble in water or in dilute acids, or precipitable from solutions which are either neutral or slightly acid. This difference of behavior is made use of in distinguishing the metals from each other. First, the last class of metals is precipitated from a slightly acid solution by H_2S, the filtrate is neutralized, and the second class is precipitated with NH_5S (solution of H_2S in NH_5O); the filtrate from this precipitate contains the first class.

Hydrosulphuric acid is recognized by its odor, as well as by the separation of black plumbic sulphide (PbS) when the gas comes in contact with paper moistened with a solution of lead. Of the

metallic sulphides, the compounds of sulphur with the alkaline metals are easily soluble in water; those with the metals of the alkaline earth are less soluble; both of these classes of metallic sulphides dissolve in water, with decomposition, forming sulphydrates and hydrates (e.g., $K_2S + H_2O = KHS + KHO$). Solutions which contain only sulphydrates, treated with $MnCl_2$ give MnS and H_2S; on the other hand, solutions of metallic sulphides (sulphydrates and hydrates) give only MnS without evolution of H_2S. All other metallic sulphides are insoluble in water. Some, as aluminic sulphide and chromic sulphide, are decomposed by water into hydrate and hydrosulphuric acid.

Solutions of metallic sulphides are not stable in the air. At first colorless, they soon turn yellow, with formation of polysulphide (K_2S_2) and metallic hydrates; the polysulphides then pass into hyposulphites ($K_2S_2O_3$), sulphites (K_2SO_3), and sulphates (K_2SO_4). Since the metallic sulphides are soluble in alcohol as well as in water, but the products of their oxidation are either insoluble or only partially soluble with difficulty in the former (e.g., $MgSO_4$), the presence of the oxygen salts resulting from oxidation can be shown by the cloudiness which ensues when concentrated aqueous solutions of metallic sulphides are shaken with excess of alcohol.*

Also many metallic sulphides insoluble in water

* Metallic sulphides may be removed by an alkaline solution of zinc chloride. Filter from the ZnS formed, exactly neutralize the filtrate with HCl, and test for the sulphur acids.

become oxidized very quickly in the presence of moist air (FeS gives Fe_2O_3 and S_2, or $FeSO_4$). All metallic sulphides become decomposed by ignition in a current of air. On the addition of hydrochloric acid, metallic sulphides evolve hydrosulphuric acid. HgS, Au_2S_3, As_2S_3 are not changed by even concentrated hydrochloric acid. Nitric acid oxidizes all metallic sulphides except mercurous sulphide. The metallic sulphides generally are by nitric acid converted into sulphates ($PbSO_4$ is insoluble); the only exceptions are Sb_2S_3 and SnS_2, which in excess of nitric acid yield insoluble oxides.

Nitrohydrochloric acid decomposes all metallic sulphides with formation of metallic chlorides. All metallic sulphides ignited, before the blowpipe, with sodic carbonate, yield sodic sulphide; this can be easily recognized by the dark spot of argentic sulphide which appears when a few drops of its aqueous solution are placed upon a bright silver coin.

A drop of this solution of sodic sulphide produces in sodic nitroprusside a violet color. With acids this solution evolves hydrosulphuric acid.

A solution of soluble metallic sulphides is recognized, in the presence of hydrosulphuric acid, by sodic nitroprusside.

Sulphuric acid H_2SO_4 (anhydride SO_3 is an asbestiform solid) is an oily liquid of specific gravity 1.843, boiling point 326° C. Fuming sulphuric acid (Nordhausen oil of vitriol) is a combination of the hydrate and the anyhydride, $H_2S_2O_7$. Concentrated sulphuric acid attracts water to itself with great energy, even from organic substances, and sepa-

rates carbon from these (reduced to coal). Sulphuric acid is the strongest of the acids. It can drive out all other acids in the wet way. Heated to redness it is driven out from its combinations by some other acids, e. g., silicic acid.

The neutral sulphates are all soluble in water, except those of barium, strontium and lead. These salts are insoluble also in dilute acids. Calcic sulphate (gypsum) is soluble with difficulty in water. All sulphates are insoluble in alcohol except a few, as ferric sulphate and hydrated chromic sulphate. Crystallized magnesic sulphate ($MgSO_4+7\,H_2O$) is soluble in alcohol only with difficulty. Only the sulphates of the alkaline metals, of barium, strontium, calcium and lead, can be heated to redness without undergoing decomposition. ($Fe_2S_3O_{12}$ yields Fe_2O_3 and SO_3; $FeSO_4$ gives Fe_2O_3, SO_3 and SO_2.)

Sulphuric acid and soluble sulphates are recognized by the white precipitate which $BaCl_2$ produces in their solutions, slightly acidulated by HCl. The presence of sulphuric acid in insoluble sulphates is shown by fusing them with Na_2CO_3, as directed (page 10) in the case of insoluble chlorine compounds. The sodic salt is dissolved in HCl and then tested with $BaCl_2$. Free sulphuric acid in presence of sulphates cannot always be recognized by the acid reaction of the solution; many neutral sulphates redden blue litmus paper. If sugar is added to the substance to be tested, and the whole be then heated in the water-bath, a brown coloration of the sugar shows the presence of free sulphuric acid. Ultramarine paper is bleached by free acids.

All sulphates treated with Na_2CO_3 on charcoal before the blowpipe, yield sodic sulphide.

Sulphurous acid H_2SO_3. The anhydride (SO_2) is a gas having the characteristic odor of burning sulphur. This gas is largely absorbed by water, with formation of hydrate. In aqueous solution the acid combines with oxygen to form sulphuric acid. It takes oxygen from the air or from bodies rich in oxygen. (PbO_2 gives $PbSO_4$; $AgNO_3$ gives Ag, NO and H_2SO_4). Compounds rich in chlorine, bromine or iodine become reduced to lower chlorides, bromides or iodides by the decomposition of water (Fe_2Cl_6, $HgCl_2$). Sulphurous acid bleaches organic colors.

Sulphurous acid is easily recognized by its odor, and by its reducing action with formation of sulphuric acid. In order to detect slight traces of sulphurous acid, the solution is heated with stannous chloride ($SnCl_2$), HCl and a drop of cupric sulphate, when black cupric sulphide separates ($SnCl_2$ becomes $SnCl_4$), or it may be known by its forming H_2S in the presence of HCl and metallic zinc.

Only the sulphites of the alkali-metals are soluble in water, all others are insoluble in water, but are soluble in acids, even in free sulphurous acid. The solutions combine energetically with oxygen, forming sulphates. All evolve sulphurous acid with HCl or H_2SO_4.

Baric chloride yields in a neutral solution of a sulphite a white precipitate insoluble in water, but easily soluble in HCl; $BaSO_4$ is separated from this solution on addition of chlorine water.

Argentic nitrate gives with the soluble sulphites

a white precipitate (Ag_2SO_3), which on heating becomes dark with separation of Ag_2. Argentic sulphite dissolves easily in HNO_3. All sulphites are decomposed at a red heat. They yield, some sulphides and sulphates (K_2SO_3), others give off sulphurous acid, leaving behind metallic oxides ($CaSO_3$). On charcoal before the blowpipe they deport themselves like sulphates and sulphides.

Hyposulphurous acid $H_2S_2O_3$. The hydrate, as well as the anhydride (S_2O_2), is unstable. They are easily decomposed into sulphur and sulphurous acid. The hyposulphites of the alkali-metals, and those of the metals of the alkaline earths, are soluble in water. The others are insoluble, but are less known, since they are easily decomposed with separation of metallic sulphides (PbS_2O_3, $Ag_2S_2O_3$, $Hg_2S_2O_3$). The hyposulphites insoluble in water dissolve in an excess of alkali-hyposulphite, with formation of double salts (e. g., $Ag_2S_2O_3+2\,Na_2S_2O_3$). The hyposulphites behave in other respects like sulphites combined with sulphur. Treated with acids they evolve sulphurous acid with precipitation of sulphur, etc. Treated with oxidizing bodies, as HNO_3, $NaClO_3$, etc., they pass wholly into sulphates; iodine alone, forms with the hyposulphites of the alkali-metals tetrathionates ($Na_2S_4O_6$) and metallic iodides. On charcoal before the blowpipe they give the reactions of the other sulphur compounds.

The salts of a regular series of oxidation compounds of sulphur, called di-, tri-, tetra- and pentathionic acids ($H_2S_2O_6$, $H_2S_3O_6$, etc.), are distinguished from the sulphates and sulphites by the fact that

their barium salts are soluble in water; from the hyposulphites they are distinguished by the fact that the baric dithionates give on decomposition with hydrochloric acid, baric sulphate, and sulphurous acid, but the barium salts of the other acids give baric sulphate, sulphur and sulphurous acid.

TABLE.

	HCl	$BaCl_2$	$BaCl_2+HCl$
$KHS+KHO$ ...	H_2S	—	H_2S
K_2SO_4	—	$BaSO_4$	$BaSO_4$
K_2SO_3	H_2O+SO_2	$BaSO_3$	H_2O+SO_2
$K_2S_2O_3$	H_2O+SO_2+S	—	H_2O+SO_2+S

Detection of Sulphur Compounds.

The presence of any sulphur compound whatever may be known by the deportment of the body under examination with Na_2CO_3 on charcoal before the blowpipe.

If a substance soluble in water is presented for examination, we first satisfy ourselves by treating a portion of it with HCl, whether metallic sulphides are present.

If this is the case, a concentrated solution of the original substance is shaken with an excess of alcohol and filtered. In the filtrate then the sulphydrates, monosulphides and polysulphides are easily distinguished by their deportment with $MnCl_2$

and with HCl. On the filter remain the combinations with H_2SO_4, H_2SO_3 and $H_2S_2O_3$. They are dissolved in water, and the neutral solution is decomposed with $BaCl_2$. By this means $BaSO_4$ and $BaSO_3$ are precipitated, BaS_2O_3 remains in solution.

The solution is filtered from the precipitate, the precipitate thoroughly washed. This *filtrate* is tested for hyposulphites by heating with HCl (precipitation of S). Dilute hydrochloric acid is then poured upon the *precipitate* on the filter. If there remains an insoluble residue, it consists of $BaSO_4$. A sulphate is thereby indicated. The acid filtrate contains $BaCl_2$ with H_2SO_3. On addition of Cl_2, H_2SO_3 is converted into H_2SO_4. Upon the addition of Cl_2, $BaSO_4$ is also precipitated from the hydrochloric acid solution of the baric chloride precipitate, when sulphites are present.

In insoluble compounds metallic sulphides are recognized by HCl. The substance is heated for some time with a concentrated solution of Na_2CO_3, and filtered, and the filtrate neutralized with HCl; this neutral solution is tested for H_2SO_4, H_2SO_3 and $H_2S_2O_3$.

Detection of the Sulphur Compounds in the presence of the Metallic Chlorides, Bromides and Iodides.

Two portions are employed, one of which is examined for the sulphur compounds, the other for the metallic chlorides, bromides and iodides. The reaction of the sulphur compounds is not destroyed by the presence of the metallic chlorides, bromides or iodides. From one portion of the original sub-

stance a neutral solution is made which is tested with $BaCl_2$ for sulphates, sulphites and hyposulphites. But with the metallic chlorides, bromides and iodides, sulphites and hyposulphites would be immediately precipitated by $AgNO_3$, if the second portion were taken in neutral solution. In order to prevent this the precipitation with $AgNO_3$ must be effected in a solution acidified with nitric acid, which, if necessary, is freed from precipitated sulphur by filtering. *

III. TRIVALENT METALLOIDS.

8. PHOSPHORUS.

At. P. = 31; Mol. P_4 = 124.
Vapor density, 4.335.

Phosphorus presents two modifications. That obtained by distillation is a white, waxy, transparent mass of crystalline structure, having sp. gr. 1.8; melting point, 44°; boiling point, 290°; ignition point, in the air, 60°. Exposed to the air it unites energetically with oxygen, evolving a peculiar odor, and inflames spontaneously. It is insoluble in water, but soluble in ether, carbonic disulphide and volatile oils. Exposed to the light it becomes dark-colored, and at the surface passes over into the other modification; long exposed to a temperature of 240°—250°, it passes wholly into the second modification. In this the phosphorus is red, and has a sp. gr. of 2.1. Does not dissolve

* Exercise in the detection of separated sulphur compounds by the acids heretofore considered. Quantitative estimation of sulphuric acid in Glauber's salt. Estimation of sulphur in copper pyrites.

in the before mentioned solvents; is not inflamed on exposure to air; but on heating to 290° is converted into the original form.

Phosphorus is a violent poison. It can be detected in poisonous substances if they be mixed in a flask with moderately concentrated sulphuric acid, and distilled off through a well cooled glass tube. The vapor is luminous in the tube.

Phosphoretted hydrogen PH_3 (gas), P_2H_4 (fluid), P_4H_2 (solid), possesses a very characteristic odor, and becomes inflamed spontaneously on exposure to the air, with formation of phosphoric acid.

Metallic phosphides may be recognized from this circumstance, that they all, with caustic potash, evolve phosphoretted hydrogen; the phosphides of the metals of the alkalies and the alkaline earths exhibit this reaction with water.

Phosphoric acid. The anhydride P_2O_5 is a white, snowy mass, which in the air powerfully attracts moisture and deliquesces. It forms three hydrates: H_3PO_4, $H_4P_2O_7$, HPO_3. These hydrates are called the ortho- (tribasic), para- or pyro- (dibasic), meta- (monobasic) phosphoric acid.

a. *Ortho-phosphoric acid* H_3PO_4, is a vitreous mass, rapidly deliquescing in the air, which, with $BaCl_2$, $AgNO_3$, and albumin, gives no precipitate. If the HNO_3, liberated from a solution of the hydrate decomposed by $AgNO_3$, is removed by addition of $NaC_2H_3O_2$, a yellow precipitate (Ag_3PO_4) is obtained. Phosphoric acid forms three classes of salts, according as one, two, or three atoms of hydrogen are replaced by metals. The salts in which only one hydrogen atom of the hydrate is replaced

by a metal, are all soluble in water, with well marked acid reaction. They yield a yellow precipitate with $AgNO_3$. Of the two other series only the alkali-compounds are soluble in water, and these have an alkaline reaction. All phosphates are easily soluble in mineral acids.

The soluble phosphates (in which at least two hydrogen atoms of the hydrate are replaced by a metal,) give, with $BaCl_2$, a white precipitate, $BaHPO_4$, which is soluble even in acetic acid; with $AgNO_3$ a yellow precipitate (Ag_3PO_4) is formed in a solution of the ortho-phosphate, which is easily soluble in HNO_3 and in NH_5O. With a clear mixture of $MgSO_4$, NH_4Cl and NH_5O, the phosphates give a crystalline precipitate, $MgNH_4PO_4$; with ferric chloride they give a bright yellow precipitate ($Fe_2P_2O_8$) which is insoluble in acetic acid.

Ammonic molybdate [$(NH_4)_2\ MoO_4$], in a weak nitric acid solution of the phosphates, gives a greenish yellow precipitate, which is soluble in excess of phosphates, and easily soluble in NH_5O. In insoluble phosphates phosphoric acid is recognized if the substance mixed with much tin is treated with concentrated nitric acid. The resulting stannous oxide removes all the phosphoric acid. This mass, insoluble in nitric acid, is dissolved in caustic soda, the solution is saturated with H_2S, acidulated with acetic acid and filtered. The tin then remains on the filter as sulphide. The phosphoric acid is free in the solution, and is easily detected by means of the magnesium mixture. When these metals, with which phosphoric acid is combined, form insoluble

sulphur compounds, it is only necessary to suspen the phosphate in water and pass H_2S through it. In this case, also, phosphoric hydrate goes into solution (NH_5S acts in like manner).

b. Pyro-phosphoric acid $H_4P_2O_7$, in the free state, gives a precipitate either with $BaCl_2$, or with $AgNO_3$, or with albumin. If a solution of the hydrate be decomposed with $NaC_2H_3O_2$, $AgNO_3$ gives a white precipitate ($Ag_4P_2O_7$). This precipitate separates also, if the solution of a pyro-phosphate be decomposed with $AgNO_3$. In other respects the pyro-phosphates are like the phosphates, and upon heating with alkalies, or with nitric acid, they easily pass into ortho-phosphates.

c. Meta-phosphoric acid HPO_3, even in the free state, gives, with $BaCl_2$, abumin or $AgNO_3$, white precipitates insoluble in acetic acid. Meta-phosphates, also, easily pass into phosphates.

TABLE.

	$BaCl_2$	$AgNO_3$ (with $NaC_2H_3O_2$)	Albumin
H_3PO_4 ..	—	Ag_3PO_4 (yellow)	—
$H_4P_2O_7$..	—	$Ag_4P_2O_7$ (white)	—
HPO_3...	BaP_2O_6	$AgPO_3$ (white)	Coagulates

In order to obtain the acid hydrates from the salts, they are decomposed by $PbC_4H_6O_4$, the precipitate is thoroughly washed, suspended in water,

treated with H_2S, filtered, and the filtrate tested, after the excess of H_2S is expelled by heat.

Phosphorous acid H_3PO_3 (anhydride P_2O_3) is decomposed on heating into phosphoric acid and phosphoretted hydrogen. Only the phosphites of the alkali-metals are soluble in water. Heated with caustic soda they yield phosphates, with evolution of H_2. Phosphorous acid is characterized by its reducing action. $AgNO_3$ and $Hg_2N_2O_6$ give with H_3PO_3, metal; H_2SO_3 yields S_2. It can be easily recognized in the presence of phosphoric acid by the precipitation of sulphur from sulphurous acid and by the blackening of mercuric oxide on heating; it is very poisonous.

Hypophosphorous acid H_3PO_2 (anhydride P_2O) is decomposed by a moist heat into phosphoric acid and phosphoretted hydrogen. The hypophosphites are all soluble in water. They yield on heating, pyrophosphates and phosphoretted hydrogen. In their reactions they closely resemble the phosphites, but are distinguished from them by the solubility of the calcium salt.

TABLE.

	$AgNO_3$	CaH_2O_2	H_2SO_3
H_3PO_4	Ag_3PO_4	Ca_2HPO_4	—
H_3PO_3	Ag	Ca_2HPO_3	S
H_3PO_2	Ag	—	S

Detection of Phosphoric Acid in the presence of the compounds previously described.

Phosphoric acid remains in solution on the precipitation of the metallic chlorides, bromides and iodides, by $AgNO_3$ from a nitric acid solution, and can be detected in the filtrate of the silver salts by carefully neutralizing with ammonic hydrate.

$BaCl_2$ precipitates from a neutral solution phosphoric acid as well as sulphuric and sulphurous acids. If the precipitate is treated on the filter with HCl, both the phosphate and the sulphite pass into solution. A residue on the filter, insoluble in HCl, indicates H_2SO_4. The hydrochloric acid solution is then divided into two portions. One is tested with chlorine water for H_2SO_3; the other heated with moderately dilute H_2SO_4, filtered from the precipitated $BaSO_4$, and finally tested with magnesium mixture for H_3PO_4.*

9. Nitrogen.

At. N. $=14$; Mol. $N_2=28$.
Vapor density, 0.927.

Nitrogen is a colorless, odorless, permanent gas, which is neither combustible nor a supporter of combustion.

Ammonia NH_3, is a gas of characteristic odor; it unites with water, hydrosulphuric acid, and acid hydrates to form ammonium compounds (salts of NH_4). Since these have a close resemblance to the

* Example for practice. Estimation of phosphoric acid in $Na_2HPO_4+12\,H_2O$.

compounds of the alkali-metals, we may best consider ammonia and its compounds with the metals.

Nitric acid HNO_3 (anhydride N_2O_5, said to be a solid crystalline mass) is a colorless liquid, sp. gr. 1.5, boiling point 86°. It readily absorbs water from the air, and is decomposed in the light with yellowish discoloration, partly, into nitryl (N_2O_4), water and oxygen. The same decomposition occurs on heating nitric acid to a higher temperature. The acid, varying in color from the yellow of nitryl to a brownish-red, is called "fuming." On addition of water the color is removed.

Dilute nitric acid is stable in the light. Nitric acid readily yields oxygen; it acts as an oxidizing agent, with formation of water and nitrous oxide (NO). Nearly all metals, except Au, Pt, Sn and Sb, are dissolved with evolution of NO to form nitrates; all the lower metallic oxides are carried up to the highest degree of oxidation (except MnO); all metallic sulphides are oxidized by it (except HgS). Sn, Zn and Fe are dissolved in cold dilute nitric acid, with formation of ammonic nitrate (NH_4NO_3). Organic substances decompose nitric acid with formation of a yellow color (indigo). Aqua regia (NOCl, NO_2Cl, Cl_2) is a mixture of nitric and hydrochloric acids. The nitrates generally are soluble in water, some in solution yield basic salts, which are insoluble in water (e. g., BiN_3O_9 gives $BiNO_4$).

The nitrates of the alkali-metals are insoluble in alcohol. They are all decomposed at a red heat. Under this treatment the nitrates of the alkali-met-

als first yield nitrites, while the others directly form metallic oxides (NH_4NO_3 gives N_2O). On charcoal before the blow-pipe the nitrates deflagrate like the chlorates, but leave behind metallic oxides or carbonates; therefore, if an alkali-nitrate be tested, there remains on the coal a residue which has an alkaline reaction when dissolved in water.

Nitric acid, like the nitrates, is best recognized by the oxidizing action of free nitric acid. Nitric acid is liberated from the nitrates by concentrated sulphuric acid. In such a mixture metallic copper is dissolved with evolution of NO. Ferrous sulphate produces a brownish-black color ($FeSO_4$ becomes $Fe_2S_3O_{12}$; the NO formed thereby being absorbed by the excess of $FeSO_4$ with a black color;) indigo becomes decolorized. The nitrogen of nitric acid can be converted into other nitrogen compounds easy of recognition; by means of zinc and sodic hydrate into NH_3; by means of zinc and a little hydrochloric acid into N_2O_3.

Nitrous acid HNO_2, is not stable. The anhydride, N_2O_3, is a bluish-green liquid which is dissipated in brown-red vapors. With water it is decomposed into HNO_3 and NO. The nitrites of the metals of the alkalies and the alkaline earths are soluble in water and alcohol; the others are little known (cobalt salts in acetic acid solution give a yellow precipitate whose composition is $Co_2K_6N_{10}O_{21}$). ($Co_2 6 NO_2 + 6 (KNO_2) +$ Aq. Sadtler.) All nitrites are decomposed by heating their aqueous solutions—more readily by heating to redness. (NH_4NO_2 yields N_2.) The solutions of the nitrites

act as deoxidizing agents. ($AuCl_3$, $AgNO_3$, $Hg_2N_2O_6$, give with nitrites a metallic precipitate; $KMnO_4$ immediately becomes decolorized). In weak acid solution nitrous acid separates the iodine from potassic iodide, and precipitates sulphur from hydrosulphuric acid. The deportment of nitrous acid in other respects is identical with that of nitric acid.

Nitrous acid can be easily recognized in presence of nitric acid by the preparation of I_2 from KI, and by the immediate discoloration of $KMnO_4$. To detect nitric in presence of nitrous acid the substance under trial is evaporated to dryness, with sodic hydrate, on the water-bath; by means of alcohol the sodic nitrate can afterwards be removed.

Nitric peroxide N_2O_4, is contained in fuming nitric acid; its presence is easily recognized by its deportment with water. The brown-red liquid on the addition of a little water becomes green, then blue (N_2O_3), and ultimately colorless.

Nitric oxide N_2O_2, is a colorless gas which forms brown fumes of nitric peroxide on exposure to the air.

Nitrous oxide N_2O, is a colorless gas bearing a close resemblance to free oxygen, but on combustion with hydrogen it leaves a residue of nitrogen.

In presence of all the before-mentioned acids, any of the series of oxygen compounds with nitrogen is easily recognizable by its deportment with ferrous sulphate, or by the separation of iodine from potassic iodide, when a weak hydrochloric acid solution is treated with zinc.

10. Boron.

At. $B = 11$; Mol. $B_2 = 22$.

Boron is a solid body which exhibits an amorphous, graphitoid and diamond-like form. It burns in the air to form boric anhydride (B_2O_3); and dissolves in sodic hydrate with evolution of H_2. Boric acid, H_3BO_3, is a crystalline, somewhat volatile, substance. When heated with excess of water considerable quantities are carried off with its vapor. The anhydride, B_2O_3, is a vitreous amorphous mass, which is not decomposed by heat. The acid in aqueous solution possesses feeble acid qualities; but melted it is one of the strongest acids, and is often used in breaking up insoluble compounds. Boric acid imparts a green color to a non-luminous flame; a weak acid solution colors turmeric paper brownish-red, which is first noticeable when the paper becomes dry. The borates of the alkali-metals are easily soluble in water, with alkaline reaction. All other salts are soluble with difficulty, but none are wholly insoluble. Moistened with concentrated sulphuric acid they color a non-luminous flame green. Dissolved in dilute hydrochloric acid they redden turmeric paper. A very decisive reaction is based upon the formation of boric fluoride (BF_3), when a mixture of borates, CaF_2 and H_2SO_4, is heated. The boric fluoride is gaseous. If the gas is conducted into alcohol, and this be lighted, it burns with a green flame; if the gas be conducted into water, boric acid is separated, and is easily recognized in the aqueous solution.

[In the course of qualitative analysis the trivalent metalloids, arsenic, bismuth and antimony, properly belonging here, are grouped with the metals, and on this account are better treated with them later.]

IV. QUADRIVALENT METALLOIDS.

11. Silicon.

Atom $Si = 28$.

Silicon is an amorphous and crystalline solid of a gray color. It is with difficulty burned in the air to form SiO_2; it dissolves in sodic hydrate with evolution of H_2.

Silicic acid H_2SiO_3, is a gelatinous mass, somewhat soluble in water. On drying it loses its water and forms the anhydride SiO_2, which is entirely insoluble in water. This anhydride occurs in nature, crystallized (quartz) and amorphous (opal).

The amorphous anhydride dissolves in alkaline liquids; the crystalline form only after fusing with alkalies. Only the silicates of the alkali-metals are soluble in water. Silicic acid is precipitated from solutions of the soluble silicates by other acids as a gelatinous hydrate. Many insoluble silicates are not decomposed by hydrochloric acid; these are fused with Na_2CO_3, and the fused mass is treated with hydrochloric acid. The silicic acid thus separated is somewhat soluble in water; in order to completely remove this (to detect the metals combined with silicic acid) the mass decomposed by

HCl is evaporated to dryness. In this way the SiO_2 becomes perfectly insoluble in water, and the metals may then be easily removed by HCl.

Silicic acid in the free state as well as in silicates is easily recognized by its not dissolving in the microcosmic salt* bead, in which it floats about as a skeleton.

Fluoric acid is a powerful solvent for SiO_2; $SiFO_4$ and H_2O are formed by the solution. A mixture of SiO_2 (or silicates) CaF_2 and H_2SO_4 evolves SiF_4 on heating.

If this is mixed with water there is formed H_2SiF_6, with separation of H_2SiO_3 (the precipitate indicates the presence of SiO_2, and consequently of F_2). The hydrofluosilicic acid is decomposed by concentrating its solution (SiF_4 and HF). Exactly neutralized with metallic oxides it forms silicofluorides of the metals (excess of alkaline compounds precipitates H_2SiO_3). Almost all silicofluorides are soluble in water; the potassium, sodium and barium salts are the most difficultly soluble. NH_5O immediately precipitates H_2SiO_3 from a solution of H_2SiF_6.

* The employment of the microcosmic salt and borax beads will be frequently alluded to when we treat of the metals. Their action is as follows: Microcosmic salt $(NaNH_4)HPO_4 + 4\,H_2O)$ gives by fusing on platinum wire a colorless glass $NaPO_3$. Borax $(Na_2Bo_4O_7 + 1\,0H_2O)$ loses its water on fusing, leaving behind a clear glass bead. Both fluxes take up, at a high temperature, metallic oxides, even from their salts, and separate from these the acid anhydride, which is either volatilized or taken up by the bead. SiO_2 is not thereby dissolved by microcosmic salt; the oxides which are taken up often impart to the bead characteristic colors.

On heating, the metallic silico-fluorides yield SiF_4, and leave behind metallic fluorides. With concentrated H_2SO_4 they yield SiF_4 and HF. The metallic silico-fluorides can be recognized by the separation of H_2SiO_3 in a drop of water, contained in a platinum capsule, which one holds in the vapor as it is evolved.

12. Carbon.

At. $C. = 12$; Mol. $C_2 = 24$.

Carbon occurs in three forms, amorphous, graphitoid, and as the diamond. It yields on burning, carbonic dioxide (CO_2) and carbonic oxide (CO).

Carbonic acid. The hydrate, H_2CO_3, is unknown. The anhydride, CO_2, is a colorless, odorless gas, of peculiar taste. Water, at ordinary pressures, dissolves about its own bulk of this gas. Of the neutral carbonates, only those of the alkaline metals are soluble in water and possess an alkaline reaction. All others are insoluble. (No carbonates of aluminium, sexivalent iron and uranium are known.) Most carbonates dissolve in free carbonic acid with formation of pyrocarbonates (*e. g.*, CaC_2O_5).

All the carbonates are decomposed by the strong mineral acids with liberation of carbonic acid, which escapes with effervescence, and can be easily recognized because it produces in calcic hydrate a white precipitate of calcic carbonate.

Carbonic oxide is a colorless gas which burns with a blue flame to form carbonic acid.

[Tin, which should be classed among the quadrivalent metalloids, will be considered under the metals.]

Testing a substance for Inorganic Acids.

1. A part of the substance is heated on charcoal before the blowpipe. Substances which deflagrate are either chlorates or nitrates.

2. A portion of the substance is fused with Na_2CO_3 on charcoal, and placed, after cooling, on a silver coin and moistened with water. A dark speck indicates S.

3. A bead of microcosmic salt is treated with the substance; silicic acid forms a skeleton in it.

4. A portion of the substance is placed in a test-tube, treated with concentrated sulphuric acid and gently heated.

a. A colorless gas is evolved:

CO_2 is odorless—recognized by means of CaH_2O_2.

SO_2, HCl, H_2S, are recognized by their odor; the latter also by its action on paper moistened with a solution of plumbic acetate.

HF etches glass, SiF_4 renders a drop of water cloudy.

b. A colored gas is evolved.

Cl_2 is a greenish yellow gas; indicates chlorates or hypochlorites.

Br_2 is reddish brown (starch); (N_2O is also brown). I_2 is violet.

c. If the mixture remains uncolored, a solution of $FeSO_4$ is carefully poured on the concentrated H_2SO_4; a brown color at the line of junction indicates nitrates.

d. Some of the substance mixed with H_2SO_4 is brought on a platinum wire into a flame, H_3BoO_3.

5. If gases which can disguise CO_2 have been observed, a separate portion of the substance is tested with dilute HCl for CO_2.

6. An aqueous extract of the substance is tested for nitrates and nitrites.

7. A portion of the substance is heated for some time with a concentrated solution of Na_2CO_3, filtered, and the filtrate neutralized with HNO_3.

This solution is divided into three parts for testing:

a. By the addition of $AgNO_3$ with excess of HNO_3, for metallic chlorides, bromides and iodides (p. 10).

b. With $BaCl_2$, without further addition of acids, for salts of H_2SO_4, H_2SO_3, $H_2S_2O_3$ and H_3PO_4 (p. 26.)

c. With turmeric paper * and addition of a little HCl for H_3BoO_3.

* In this course it is taken for granted that the acids are combined only with the metals of the alkalies and alkaline earths. Further on it will be shown what modifications are necessary in the presence of many metals. During the exercises in the detection of acids, quantitative estimations of SiO_2 in natrolite and feldspar, and of CO_2 in calcite, may be undertaken.

METALS.

For the purpose of analytical chemistry, the metals may be arranged in the following groups:

I. Metals which are not precipitated by H_2S either from an acid or ammoniacal solution (metallic sulphides soluble in water).

(A). Metals whose carbonates are soluble in water (alkali-metals).

(B). Metals whose carbonates are insoluble in water (metals of the alkaline earths).

II. (C). Metals which are not precipitated by NH_5S from acid solutions, but which are precipitated from solutions neutralized with NH_5O (ammonic sulphide group).

III. Metals which are precipitated by H_2S even from slightly acid solutions (hydrosulphuric acid group).

(D). Metallic sulphides insoluble in NH_5S.

(E). Metallic sulphides soluble in NH_5S.

(A). ALKALI-METALS.

1. Potassium.

$K = 39.1$.

Is a silver-white, soft metal, of .865 sp. gr., which melts at 62°. It oxidizes in the air so rapidly that it must be kept under naphtha. Water is decomposed by potassium, even at ordinary temperatures, with evolution of H_2 (formation of KHO). The potassium is thereby ignited, burning with a violet flame. Almost all potassium compounds are soluble in water. Solutions of potassium salts which are acidulated with HCl, and are not too dilute, will give precipitates with $PtCl_4$, H_2SiF_6 and $C_4H_6O_6$ (tartaric acid).

Potassio-platinic chloride, K_2PtCl_6, is a yellow crystalline salt, which is difficultly soluble in water, absolutely insoluble in ether-alcohol, and breaks up at a red heat into chlorine, platinum and potassic chloride. Potassio-silicic fluoride, K_2SiF_6, is a gelatinous precipitate which becomes distinctly visible upon addition of alcohol. Hydro-potassic tartrate, $KC_4H_5O_6$ (acid potassic tartrate), separates only from very concentrated solutions; rubbing the sides of the vessel hastens its formation. Heated to redness, hydro-potassic tartrate leaves a carbonaceous residue having an alkaline reaction. All potassium compounds yield a similar violet color when brought on a platinum wire into a non-luminous flame; when seen through a blue glass, or a flattened glass flask containing indigo-solution (1 part of indigo, 8 parts of

H_2SO_4, 1500 parts of H_2O) the flame appears reddish-violet. The violet potassium flame has in its spectrum a characteristic red and a violet line.

2. Sodium.

$Na = 23$.

Is a silver-white metal; sp. gr. 0.972; melting point 90°; must be kept under naphtha. Easily decomposes water, but inflames only when the water is heated to above 60°, or when its motion is impeded, for instance on ice. Ignited it burns with a yellow flame. The sodium compounds are for the most part more easily soluble than the potassium salts. Na_2SiF_6 is difficultly soluble, potassic metantimonate ($Na_2H_2Sb_2O_7$) is alone insoluble.

This salt is precipitated when the alkaline solution of a sodium salt is decomposed by a freshly prepared solution of potassic antimonate. All sodium compounds give the flame a yellow color, which cannot be seen through blue glass or the indigo prism. The spectrum of the sodium flame consists of a bright yellow line.

3. Ammonium.

$NH_4 = 18$.

Isolated is said to be a blue liquid, and to form an amalgam with mercury.

The ammonium compounds are formed when ammonia enters into any combination whatever with water, hydrosulphuric acid, acids or salts (*e.g.*, $NH_3 + H_2O = NH_5O = NH_4 \cdot HO$; $NH_3 + H_2SO_4 = NH_4 \cdot HSO_4$).

Almost all ammonium salts are soluble in water. Ammonio-platinic chloride ($(NH_4)_2PtCl_6$) is a yellow precipitate, which is liable to be mistaken for the corresponding potassium compound, but which can be distinguished from the latter by the fact that it leaves, at a red heat, pure platinum (water dissolves from the ignited residue no metallic chloride), and yields NH_3 when warmed with CaH_2O_2. The ammonium salt, $NH_4 \cdot C_4H_5O_6$, corresponding to acid potassic tartrate, is also soluble with difficulty, but leaves behind at a red heat a carbonaceous residue which is not alkaline. All ammonium compounds by boiling with KHO, or by heating with CaH_2O_2, are decomposed with evolution of NH_3. This gas is easily recognized by its odor, and by the white cloud which it forms with the vapor of HCl. If NH_3 is placed on a paper which has been moistened with a neutral aqueous solution of $Hg_2N_2O_6$, there appears a black spot ($Hg_2NO_3 + 2\,NH_5O = NH_2Hg_2NO_3 + NH_4NO_3 + 2\,H_2O$).

NH_3 is soluble in water. The aqueous solution yields with $HgCl_2$ a white precipitate (HgH_2NCl); with a solution of HgI_2 in KI an aqueous solution of NH_3 in the presence of KHO gives a brown precipitate ($HgH_2NI + HgO$).

All ammonium salts are completely volatilized by ignition. Many deposit a sublimate of the unchanged salt in the colder part of the tube $(NH)_4Cl$, $(NH_4)_2CO_3$, $(NH_4)_2SO_4$, but some are thereby completely decomposed $(NH_4)_2HPO_4$, $(NH_4) \cdot NO_3$. The volatilized ammonium salts color a non-luminous flame violet, like the potassium compounds.

Detection of Potassium, Sodium and Ammonium.

1. A portion of the dry substance is mixed with CaH_2O_2 and heated. The evolution of NH_3 indicates ammonium salts.

2. After the ammonium compounds of a second portion of the original substance have been expelled by ignition, the residue is brought on a platinum wire into a non-luminous flame. Potassium colors violet, sodium yellow. Sodium can disguise the potassium flame. Therefore the sodium flame is examined through an indigo prism. Only when potassium is present can the flame be seen through this.*

(B). METALS OF THE ALKALINE EARTHS.

4. Barium.

Ba = 137.

Barium is a slightly yellow metal which decomposes water. Baric oxide, BaO, is an amorphous white mass, which unites with water energetically, forming a crystallizable hydrate, $BaH_2O_2 + 8\ H_2O$.

The aqueous solution of this hydrate has a strong alkaline reaction (baryta-water). Only a few barium salts are insoluble in water, but these dissolve in hydrochloric acid with the single exception of baric sulphate. Carbonates of the alkali-metals precipitate $BaCO_3$. Sulphuric acid and soluble sulphates throw down all the barium as $BaSO_4$, a white, finely gran-

* Estimation of sodium in $Na_2HPO_4 + 12\ H_2O$.

ular precipitate which is not soluble in HCl, and is decomposed only by protracted boiling with $(NH_4)_2CO_3$ or by fusing with Na_2CO_3, thereby forming baric carbonate and alkali-sulphate. Hydrofluosilicic acid (H_2SiF_6), neutral potassic chromate, K_2CrO_4, and ammonic succinate ($(NH_4)_2C_4H_4O_4$) yield precipitates in neutral solutions of barium salts. $BaCl_2$ and BaN_2O_6 are insoluble in absolute alcohol.

Barium salts color the flame greenish-yellow; this flame gives a spectrum which is very rich in yellow and green lines.

5. Strontium.

$Sr = 87.6$.

Strontium closely resembles barium. In the following particulars their compounds differ: $SrSO_4$ is soluble to such an extent that an aqueous solution of strontic sulphate can be employed for the detection of barium. $SrSO_4$ naturally separates more slowly than $BaSO_4$; on the addition of alcohol all the $SrSO_4$ is precipitated. Even in the cold, strontic sulphate is decomposed by $(NH_4)_2CO_3$; H_2SiF_6, K_2CrO_4, $(NH_4)_2(C_4H_4O_4)$ produce no precipitates in solutions of strontium. SrN_2O_6 is insoluble, $SrCl_2$ is soluble in absolute alcohol. Strontium compounds color the flame a beautiful red; the flame presents, in the spectrum, a characteristic blue line, together with red lines.

6. Calcium.

$Ca = 40$.

The metal resembles Ba and Sr; its oxide is white; its hydrate is also white and amorphous, soluble in water (1 part of CaH_2O_2 requiring 778 parts of H_2O). Calcium salts are very much like the strontium salts in their solubility, with the following exceptions; sulphuric acid and soluble sulphates precipitate $CaSO_4$ only from concentrated solutions, but from dilute solutions only on the addition of alcohol. Oxalic acid ($C_2H_2O_4$) and soluble oxalates ($(NH_4)_2C_2O_4$) throw down the calcium completely as CaC_2O_4. The precipitate is soluble in HCl, but is insoluble in $C_2H_4O_2$. It can also be separated out again from a hydrochloric acid solution by $NaC_2H_3O_2$.

Flame yellowish-red. The spectrum presents, besides red, yellow and green lines, a characteristic violet line.

7. Magnesium.

$Mg = 24$.

This metal is silver-white, burning in the air with a dazzling flame to white MgO. The oxide is insoluble in water, but the hydrate, MgH_2O_2 is somewhat soluble (1 part MgH_2O_2—5000 parts of H_2O); the solution has an alkaline reaction. Magnesium salts are almost all soluble. MgH_2O_2 is precipitated from these solutions by KHO, NaHO, BaH_2O_2, etc. The presence of ammonium salts prevents this

precipitation; the magnesium compounds form with salts of ammonium, double salts, which are not decomposed by alkalies at ordinary temperatures (*e.g.*, $2 MgSO_4 + 4 (NH_4)Cl = MgSO_4 \cdot (NH_4)_2SO_4 + MgCl_2 \cdot 2 NH_4Cl$). Ammonic hydrate precipitates only half of the magnesium held in a solution, the other half remains in solution as a double salt.

The precipitated magnesic hydrate can be easily redissolved by means of ammonium salts (*e.g.*, by ammonic chloride). Acid solutions of magnesium and those containing ammonium salts give with NH_5O no precipitate; $(NH_4)_2CO_3$ fails to separate out $MgCO_3$ even at a boiling temperature.

Na_2CO_3 at the boiling point throws down all the magnesium as carbonate, of course only from solutions which are free from ammonium salts. Soluble phosphates precipitate from magnesium solutions $MgHPO_4$ (soluble in much water), but in the presence of ammonium compounds, $MgNH_4PO_4$. This crystalline precipitate is characteristic of magnesium. It is difficultly soluble in water, easily soluble in acids, insoluble in ammonic hydrate. The flame is not colored by magnesium compounds. Magnesium salts glow when heated intensely before the blowpipe. Magnesic oxide ignited on charcoal, then moistened with CoN_2O_6 and again heated, becomes flesh-red.

Detection of the Alkaline Earths and Alkalies in presence of each other.

The solution, which may contain Ba, Sr, Ca, Mg, Na and K, is treated with NH_4Cl, and precipitated by

$(NH_4)_2CO_3$, with addition of NH_5O,* the precipitate placed on a filter and thoroughly washed.

1. *Precipitate* is dissolved off from the filter in dilute HCl. A portion of this solution is tested with calcic sulphate for Ba and Sr.

a. If neither Ba nor Sr has been found, treat the remainder of the hydrochloric acid solution with ammonic oxalate and ammonic hydrate, any calcium present will then be precipitated.

b. If Ba or Sr has been found, the remainder of the hydrochloric acid solution is neutralized by NH_5O, and there is precipitated by a *neutral* solution of K_2CrO_4 only $BaCrO_4$. After filtering, the filtrate is tested with H_2SO_4 for Sr. To complete the precipitation of the $SrSO_4$ it is allowed to stand for a while, filtered, the filtrate is neutralized by NH_5O and tested as above for Ca.

2. *Filtrate.* A portion is tested with Na_2HPO_4 for magnesium.

a. If no magnesium is present, the remainder of the filtrate is evaporated to dryness, the residue ignited until the ammonium salts have been driven off and then tested by the flame for K and Na.

b. If Mg has been detected, it must be removed before K and Na are tested for. For this purpose the remainder of the filtrate is evaporated, and the

* Theoretically $(NH_4)_2CO_3$ alone is sufficient, but the solution of the commercial ammonic carbonate contains a salt having the formula $(NH_4)_4C_3O_8$, a sesqui-carbonate of ammonium. By the former reaction, the CO_2 present in excess might form pyrocarbonate, hence the addition NH_5O. We, always, for brevity, write $(NH_4)_2CO_3$.

residue ignited to expel the ammonium compounds. The ignited residue is dissolved in H_2O and a drop of HCl (MgO) and the MgH_2O_2 thrown down by BaH_2O_2. After filtration the barium compounds are removed from the filtrate by $(NH_4)_2CO_3$ and NH_5O, again filtered, the filtrate evaporated to dryness, ignited, and tested finally for K and Na.*

(C). METALS OF THE AMMONIC SULPHIDE PRECIPITATE.

1. *METALS WHICH ARE PRECIPITATED BY* NH_4S *AS HYDRATES.*

8. ALUMINIUM.

$Al_2 = 55$.

This metal is tin white; sp. gr. 2.67; does not oxidize in the air at ordinary temperatures; at a red heat it rapidly oxidizes, forming Al_2O_3. It is soluble in dilute acids and alkalis ($Al_2K_6O_6$). Aluminic oxide is a white, earthy mass, which is easily soluble in acids. After intense ignition it is insoluble; by fluxing with $KHSO_4$ it is rendered soluble. The oxide is soluble also in caustic alkalis. The hydrate is ordinarily a horny amorphous mass, but it is also found in crystals (hydrargillite), and from the solution of Al_2O_3 in NaHO it is precipitated in the crystalline form by CO_2. The salts of aluminium are colorless. They are decomposed at a red heat with

* Quantitative estimation of Ca in calcite. Estimation of Ca and Mg in dolomite.

loss of acid. They are for the most part soluble in water.

KHO, BaH_2O_2, NH_5O, NH_5S, $(NH_4)_2CO_3$, $BaCO_3$, precipitate from aluminium solutions $Al_2H_6O_6$, soluble in excess of KHO or BaH_2O_2. They are reprecipitated from these solutions by NH_4Cl, CO_2 or a little HCl. Tartaric acid prevents these precipitations. By boiling a neutral aluminium solution with $Na_2S_2O_3$, $Al_2H_6O_6$ is precipitated ($Al_2S_3O_{12} + 3\,Na_2S_2O_3 + 3\,H_2O = Al_2H_6O_6 + 3\,Na_2SO_4 + 3\,S_2$).

Of the insoluble aluminium salts the phosphate only is spoken of. This salt behaves like aluminic hydrate. It is soluble in KHO, is precipitated from this solution by NH_4Cl. Tartaric acid hinders this precipitation.

It is distinguished from $Al_2H_6O_6$ by its insolubility in $C_2H_4O_2$. From an alkaline ammoniacal solution of $Al_2P_2O_8$, decomposed by tartaric acid, there falls $MgNH_4PO_4$ on addition of magnesium mixture ($MgSO_4NH_4Cl$).

Aluminium compounds, heated to redness on charcoal before the blowpipe, moistened with CoN_2O_6 and again heated to redness, yield a blue mass.*

9. Chromium.

$Cr = 53$; $Cr_2 = 106$.

Metallic chromium is a gray powder, soluble in HCl, H_2SO_4 and KHO. In its compounds the single atom is bivalent, the double atom is sexivalent ($2\overset{\text{II.}}{Cr} = \overset{\text{VI.}}{Cr_2}$). Of the compounds of bivalent chromium, we have chromic acid (CrO_3), and of those of sexiv-

* Analysis of potash alum.

alent we have chromoxide (Cr_2O_3) and their combinations to consider.

A. *Chromoxide*, Cr_2O_3, is a dark green powder; the hydrate is grayish green. The salts of sexivalent chromium are violet; their solutions turn green on boiling. The compounds of Cr_2 deport themselves in a manner quite analogous to those of the aluminum salts. They differ as follows: The dilute solution of $Cr_2H_6O_6$ in KHO precipitates $Cr_2H_6O_6$ on boiling. In a great excess of NH_5O, $Cr_2H_6O_6$ dissolves, the solution being violet. Cr_2O_3 easily passes over into CrO_3. If the compounds of Cr_2 are fused on platinum wire, with Na_2CO_3 and KNO_3, a *yellow* bead of Na_2CrO_4 is formed. In alkaline solution Cr_2O_3 is easily converted into K_2CrO_4 by Cl_2, NaClO, or $KMnO_4$.

B. *Chromic acid*, CrO_3 (hydrate H_2CrO_4), yields red crystals, is easily soluble in H_2O, and is decomposed at a red heat, leaving behind a residue of Cr_2O_3. The neutral chromates are yellow, the acid (pyrochromates, *e.g.*, $K_2Cr_2O_7$) are red. Only the chromates of K, Na, NH_4, Sr, Ca and Mg are soluble in water. The silver salt (Ag_2CrO_4) has a characteristic red color. By heating with HCl or H_2SO_4; CrO_3 is decomposed (formation of Cr_2Cl_6 or $Cr_2S_3O_{12}$ with evolution of Cl_2 or O_2). The yellow solution is thereby changed first to red, then brown, and finally green. The deoxidation is more easily accomplished by H_2S (formation of H_2O with separation of S_2), H_2SO_3 (formation H_2SO_4), alcohol (C_2H_6O) (formation of aldehyde—C_2H_4O and acetic acid—$C_2H_4O_2$)

Beads of borax and microcosmic salt are colored by chromium compounds emerald green before the blowpipe.

2. *METALS WHICH ARE PRECIPITATED BY* NH_5S *AS METALLIC SULPHIDES.*

10. IRON.

$Fe=56$; $Ffe^{*}=112$.

The metal is gray; sp. gr. 7.8. It oxidizes in moist air to $Fe_2H_6O_6$; at a higher temperature to Fe_3O_4. Dilute HCl and H_2SO_4 dissolve the metal with evolution of H_2 and formation of $FeCl_2$ or $FeSO_4$. Concentrated H_2SO_4 yields on heating $Fe_2S_3O_{12}$, and SO_2. Dilute HNO_3 yields when cold FeN_2O_6 and NH_4NO_3, when heated $Fe_2N_6O_{18}$ and NO. Commercial iron contains C, Si, P, S, etc. Iron is dissolved for examination of the residue in H_2O and I_2 or in a neutral solution of $CuCl_2$ or by electrolysis in very dilute hydrochloric acid, in which the iron serves as the positive pole.

The iron atom, with the combining weight 56, is bivalent and trivalent; as trivalent it appears only in double atoms which are then sexivalent, hence ($2\overset{\text{II.}}{Fe}=\overset{\text{VI.}}{Fe_2}$). Bivalent iron forms ferrous salts (salts of the protoxide of iron); the sexivalent the ferric compounds (compounds of the peroxide).

A. *Ferrous oxide* forms a white hydrate, FeH_2O_2, which quickly turns brown on exposure to the air. The anhydrous salts of bivalent iron are white, the hydrous bright green. In aqueous solution they absorb O_2 from the air and precipitate $Fe_2H_6O_6$ (*e. g.*, $6\,FeSO_4+3\,H_2O+3\,O=2\,Fe_2S_3O_{12}+Fe_2H_6O_6$). KHO and NH_5O precipitate FeH_2O_2; tartaric acid prevents the precipitation.

* For convenience, Ffe is printed Fe_2.

NH_5S precipitates black FeS, which rapidly oxidizes in the air ($FeSO_4$ or $Fe_2H_6O_6$) and dissolves very easily in HCl. KCy precipitates reddish brown $FeCy_2$, which is soluble in KCy by the formation of K_4FeCy_6. K_4FeCy_6 gives, with ferrous salts, a white precipitate, $K_2Fe_2Cy_6$, which very quickly turns blue on exposure to the air. $K_6Fe_2Cy_{12}$ precipitates Prussian blue, $Fe_3Fe_2Cy_{12}$, which is insoluble in HCl, and is decomposed into $Fe_2H_6O_6$ and K_4FeCy_6, on boiling with KHO. Metallic Ag and Au are precipitated from $AgNO_3$ and $AuCl_3$ by ferrous salts.

By means of oxidizing substances as Cl_2, NaClO, HNO_3, Fe is changed into Fe_2.

B. *Ferric oxide* is red; the hydrate, $Fe_2H_6O_6$, is brown; it closely resembles Al_2O_3 and Cr_2O_3 in its deportment. It differs in the following particulars: $Fe_2H_6O_6$ is insoluble in KHO; NH_5S precipitates from solutions of Fe_2 black FeS (separation of S); KCy precipitates $Fe_2H_6O_6$ (evolution of HCy) which is insoluble in excess of KCy; K_4FeCy_6 precipitates Prussian blue ($(Fe_2)_2Fe_3Cy_{18}$).

KCyS yields a blood red color, which does not disappear on addition of HCl ($Fe_2Cy_6S_6$). Ammonic succinate precipitates from a neutral solution brown ferric succinate. Sodic acetate colors a neutral solution dark red (the color is destroyed by HCl), and on boiling with a little acetic acid all the iron separates as $Fe_2H_6O_6$.

By means of deoxidizing substances, as Fe, H_2S, H_2SO_3, $Na_2S_2O_3$, the compounds of sexivalent iron easily pass over into those of bivalent iron (*e. g.*, $Fe_2Cl_6 + 2\,Na_2S_2O_3 = 2\,FeCl_2 + 2\,NaCl + Na_2S_4O_6$).

Iron compounds color beads of microcosmic salt and borax green in the reducing flame; in the oxidizing flame they become red; on cooling they become colorless.*

TABLE.

	$FeSO_4$	Fe_2Cl_6
KHO	White (green)	Brown
KCy	$FeCy_2$ (sol. in ex.)	$Fe_2H_6O_6$ (insol. in ex.)
K_4FeCy_6 ...	White	Blue
$K_6Fe_2Cy_{12}$ ..	Blue	—
KCyS	—	Red.

11. Manganese.

$Mn = 55$; Mmn† $= 110$.

The metal is of a clear gray color, very brittle, and fusible with great difficulty. It dissolves in acids to form compounds in which the atom is bivalent. Manganese is bivalent and sexivalent like iron, $2 \overset{\text{II.}}{Mn} = \overset{\text{VI.}}{Mn_2}$. It forms five oxidation products: MnO, Mn_2O_3, MnO_2, MnO_3, Mn_2O_7. All form by ignition in the air Mn_3O_4, all are dissolved in HCl or H_2SO_4 with formation of salts of bivalent Mn; all the oxygen compounds containing more oxygen

* Quantitative analysis of green vitriol. † Mmn is for convenience written Mn_2.

than the protoxide evolve Cl_2 or O_2 on treatment with these acids.

In hydrochloric solution manganese always exists in the form of manganous salts. The *manganous* salts are of a faint rose-red color. KHO and NH_5O precipitate white MnH_2O_2, which quickly becomes brown in the air ($Mn_2H_6O_6$). This brownish precipitate is dissolved in oxalic acid ($C_2H_2O_4$) to purple $K_2Mn_2C_8O_{16}$. NH_4Cl prevents this precipitation by NH_5O, through the formation of double salts resembling those of magnesium. Alkaline carbonates throw down white $MnCO_3$; $BaCO_3$ does not produce any separation. NH_5S throws down flesh-colored MnS, soluble in acetic acid, quickly oxidizing in the air. NaClO (or Cl_2 and NH_5O) separates out from manganous solutions brown peroxide (MnO_2). On heating a manganese solution with excess of minium (Pb_3O_4) and concentrated HNO_3, the fluid assumes a purplish-red color (formation of $HMnO_4$, hydrated permanganic acid).

Manganous compounds do not become manganic by heating with HNO_3. Manganic salts are purplish-red; by heating with HCl they become manganous salts with evolution of Cl_2. *Peroxide of manganese* (MnO_2) is a blackish-brown body which is scarcely dissolved by dilute acids; concentrated acids dissolve this oxide more readily when their action is aided by addition of some $C_2H_2O_4$ ($MnO_2 + C_2H_2O_4 = MnO + H_2O + 2\,CO_2$).

Manganates (salts of manganic acid) are green. Upon fusing a manganese compound with KNO_3 and Na_2CO_3 a *green* mass is produced. The manganates

of the alkalis (K_2MnO_4) are alone soluble in water. Their green solution becomes in the air red, with separation of MnO_2 and formation of permanganates $KMnO_4$= mineral-chameleon; $3K_2MnO_4 + 2H_2O = 2KMnO_4 + MnO_2 + 4KHO$.

Manganese compounds color a microcosmic bead in the oxidizing flame, amethyst, in the reducing flame the bead becomes colorless.

12. Zinc.

$Zn = 65$.

This metal is bluish-white, has a sp. gr. of 6.8, and melts at 412°; at a higher temperature it is volatile. In dry air it is not oxidized at ordinary temperatures, but in presence of H_2O forms ZnH_2O_2, which readily absorbs CO_2. Ignited in the air it burns away with pale blue flame, with formation of white ZnO. HCl and H_2SO_4 dissolve the metal with evolution of H_2; dilute HNO_3 dissolves zinc with formation of NH_4NO_3 and evolution of N_2O ($12Zn + 30HNO_3 = 12ZnN_2O_6 + 2NH_4NO_3 + 11H_2O + N_2O$). Caustic alkalis dissolve the metal with evolution of $H_2(ZnK_2O_2)$.

Zinc salts are almost all colorless. Most of them are soluble in water, all in acids. KHO, NaHO, NH_5O, precipitate ZnH_2O_2, which is soluble in excess of the precipitant (ZnK_2O_2, $Zn(NH_4)_2O_2$, etc.). From this solution zinc is not precipitated by NH_4Cl; but white ZnS is precipitated by H_2S. NH_5O produces in zinc solutions which contain NH_4Cl, not a trace of precipitate; double salts are produced, as in the

cases of Mg and Mn. But this zinc solution is distinguished from the magnesium solution by the fact that no precipitate is produced in it by Na_2HPO_4. Zinc solutions which are not decomposed by ammonium salts give a precipitate of $ZnHPO_4$ with Na_2HPO_4. Alkali-carbonates precipitate $ZnCO_3$. $BaCO_3$ forms no precipitate. NH_5S and H_2S give in neutral or acetic solutions a precipitate of ZnS. KCy precipitates $ZnCy_2$, which is soluble in excess of KCy (ZnK_2Cy_4). From this solution the Zn is precipitated by K_2S.

Zinc salts give on charcoal before the blowpipe, either alone or with $NaCO_3$ or KCy, a white slag, which is not volatile, and is yellow while warm. Moistened with CoN_2O_6 and heated to redness, on charcoal, the residue becomes green.

13. Nickel.

Ni = 58.74; Nni * = 117.48.

Nickel is white with a tinge of yellow. It is not oxidized in the air at ordinary temperatures. In acids it dissolves with formation of bivalent nickel. Only the bivalent metal atom forms salts; the sexivalent appears only in Ni_2O_3, which deports itself as à peroxide. Nickel protoxide, NiO, is gray, and remains unchanged at a red heat. Anhydrous nickel salts are yellow; hydrous are green.

Caustic alkalis precipitate from solution of nickel salts green hydrate, NiH_2O_2, which is insoluble in excess of the alkalis. NH_5O also precipitates NiH_2O_2,

* Nni is for convenience written Ni_2.

but the precipitate is soluble in excess (formation of NH_4NiH_2NO). In solutions which contain NH_4Cl, NH_5O forms no precipitate.

Alkali carbonates precipitate $NiCO_3$, which is soluble in $(NH_4)_2CO_3$.

$BaCO_2$ produces no precipitate in the cold. H_2S and NH_5S precipitate the nickel from an ammoniacal solution as black NiS; if separated at once this is very soluble in dilute HCl; but a trace dissolves only in yellow ammonic sulphide, and then colors the filtrate brown by the ammonic sulphide precipitate. KCy precipitates bright green $NiCy_2$, which is soluble in excess of KCy; from this solution all the nickel is precipitated again by dilute HCl as $NiCy_2$, even upon boiling. Nickel is also precipitated from the solution of $NiCy_2$ in KCy, by boiling with HgO; but no precipitate is produced in this solution by K_2S(KHS and KHO). Oxalic acid precipitates NiC_2O_4, which is soluble in NH_5O; after standing for a short time exposed to the air all the nickel separates from this solution in the form of green crystals ($NiNH_3C_2O_4$). NaClO produces in neutral nickel solutions a blackish-brown precipitate of Ni_2O_3. $NiCO_3$ with Cl_2 and H_2O also gives Ni_2O_3.

A *borax bead* (but not a microcosmic) is colored yellowish-red in the oxidizing flame by nickel salts; in the reducing flame, especially upon addition of tin (tinfoil), the bead becomes gray (metallic nickel).

14. Cobalt.

$Co = 58.74$; Cco * $= 117.48$.

The metal closely resembles nickel. It is bivalent and sexivalent, and both atoms form salts. The compounds of the bivalent atom closely resemble those of nickel. They differ in the following particulars: Cobalt protoxide (CoO) is grayish green; it yields when heated to redness in the air black Co_3O_4. The anhydrous salts of cobalt are blue, the hydrous are red. CoH_2O_2 is bluish red. The solution of cobalt salts in excess of NH_5O turns brown on exposure to the air, and forms cobalt-amines. The solution of CoC_2O_4 in NH_5O throws down a red precipitate only after standing a long time. KCy dissolves $CoCy_2$, which is precipitated again from this solution by HCl. If the solution is boiled, however, potassio-cobaltic-cyanide is formed, and HCl no longer produces a precipitate ($2\,CoK_2Cy_4 + 4\,KCy + 2\,H_2O = Co_2K_6Cy_{12} + 2\,KHO + 2\,H$). From this boiled solution the cobalt is not precipitated either by K_2S or by HgO. KNO_2 produces in an acetic acid solution of cobalt salts a yellow precipitate of potassio-cobaltic nitrite ($2CoCl_2 + 12KNO_2 + 2C_2H_4O_2 = 2\,C_2H_3KO_2 + 4\,KCl + H_2O + 2\,NO + Co_2K_6N_{10}O_{21}$). $NaClO$ or Cl_2 and NH_5O precipitate from cobalt salts cobalt oxide, a brown body which possesses weak basic properties, but which deports itself as a peroxide in the presence of HCl, H_2SO_4, and $H_2C_2O_4$.

Borax and microcosmic beads are colored a beau-

* Cco is here written Co_2.

tiful blue both in the inner and outer flames by cobalt compounds.

Analysis of the ammonic-sulphydrate precipitate.

If one decomposes a neutral or slightly acid solution of a substance which contains only the metals heretofore described, with NH_5O to alkaline reaction, and warms it for some time with NH_5S in slight excess, whether a precipitate forms or not, then filters and washes the precipitate with water to which some NH_5S has been added, he will have upon the filter a precipitate which may contain NiS, CoS, MnS, ZnS, FeS, $Al_2H_6O_6$ and $Cr_2H_6O_6$. The precipitate is treated with cold dilute HCl upon the filter.

1. *Residue upon the filter.* If this is black it can only consist of NiS and CoS (if it is not colored it contains only sulphur, and is then quite volatile on being heated). A part of the residue is placed in the bead of microcosm salt; if this is then blue before the blowpipe, Co is indicated. The remainder of the dark residue is dissolved in a little aqua regia, the excess of acid is evaporated, and the solution neutralized with NaHO and treated with KCy till the precipitate at first appearing is dissolved. The solution is then boiled for some time, and HCl is added to acid reaction, when $NiCy_2$ separates if Na is present.

2. *Hydrochloric acid solution.* This contains still Mn, Zn, Fe, Al_2, Cr_2. The iron is next oxidized by boiling the solution with a few drops of HNO_3, and after addition of NH_4Cl, precipitated with NH_5O in slight excess, filtered and washed.

a. The *filtrate* contains Mn and Zn. Both are precipitated again by NH_5S; the precipitate is collected on a filter and a part of it tested for Mn by heating it together with Na_2CO_3 and KNO_3 on platinum foil (green enamel), or with minium and nitric acid (reddish-purple solution). The remainder of the precipitate is dissolved in dilute HCl, $NaC_2H_3O_2$ is added, and this acetic acid solution is treated with H_2S. Only white ZnS falls.

b. *Precipitate.* In this, Fe_2, Al_2 and Cr_2 are to be searched for. This precipitate is to be dissolved in HCl and again thrown down by NaHO in the cold. By this means $Fe_2H_6O_6$ is separated out (tested for by K_4FeCy_6). The alkaline solution contains $Al_2Na_6O_6$ and $Cr_2Na_6O_6$. Both metals are thrown down as hydrates by boiling the alkaline solution with NH_4Cl. The washed precipitate, fused with Na_2CO_3 and KNO_3, is tested upon platinum foil for Cr; a yellow fused mass shows the presence of this metal. The fused mass is dissolved in water. Any residue which may remain is Al_2O_3 (dissolved in HCl and precipitated by NH_5O). Dissolve the whole of the fused mass and treat the solution with warm $(NH_4)_2CO_3$. The $Al_2K_6O_6$ (KNO_3 can be reduced to K_2O) contained in the solution will be decomposed and $Al_2H_6O_6$ thrown down.

Since in this system of analysis an acid solution of the original substance must first be neutralized by NH_5O for the production of the ammonic sulphydrate precipitate, all the aforesaid metals and those compounds of the alkaline earths are thrown down which are separable by ammonia, unchanged from an acid solution. This indicates especially the

presence of phosphates of the metals of the alkaline earths. It must be borne in mind that the phosphates of Al_2 and Cr_2 behave like the hydrates of the same metals, and also that $Al_2P_2O_8$ and $Cr_2P_2O_8$ can be contained in the ammonic sulphydrate precipitate. When such phosphates are present, the precipitate must be dissolved in hydrochloric acid, next the solution is to be oxidized by HNO_3, precipitated by NH_4Cl and NH_5O, then besides $Fe_2H_6O_6$, $Al_2H_6O_6$ and $Cr_2H_6O_6$, the phosphates must be looked for. The precipitation of Fe_2, Al_2 and Cr_2 can be prevented by tartaric acid, but the phosphates of Ba, Sr, Ca and Mg will be thrown down in the presence of tartaric acid. A part of the hydrochloric acid solution of Fe_2, Al_2, Cr_2, is to be treated with tartaric acid and rendered alkaline by NH_5O.

1. There is no precipitate.

In this case there are no phosphates of the alkaline earths present. But in order to see whether Al_2 or Cr_2 were perhaps united with phosphoric acid, add to the ammoniacal solution containing tartaric acid a clear mixture of $MgSO_4$, NH_4Cl and NH_5O. If $MgNH_4PO_4$ falls, the presence of phosphoric acid is proved.

2. There is a precipitate.

In this case the whole hydrochloric acid solution of Fe_2, Al_2, Cr_2, must be treated with tartaric acid and ammonia, the residual precipitate must be collected in a filter and washed.

a. Precipitate.

Phosphates of Ba, Sr, Ca, and Mg. Dissolve this in HCl, add a little Fe_2Cl_6, neutralize with Na_2CO_3, so

that the precipitate may be again dissolved, add $NaC_2H_3O_2$, and boil the not too concentrated solution. All the iron and all the phosphoric acid will now be precipitated.

a. The filtrate may be tested, as previously directed, for Ba, Sr, Ca, Mg.

B. The precipitate is to be dissolved in HCl, treated with NH_5O and NH_5S, and the filtrate from the FeS tested for phosphoric acid.

b. Filtrate.

This is to be next tested for phosphoric acid by the well known magnesium mixture. The phosphoric acid thus detected will probably be in combination with Al_2 or Cr_2. Whether this is found or not, the solution is to be evaporated, the residue ignited until the tartaric acid is decomposed, and the coal is then to be heated with concentrated hydrochloric acid. Fe, Al and Cr become again dissolved, oxidize with HNO_3 and test for the three metals, as previously directed.

The fluorine compounds of Ba, Sr, Ca and Mg, can be recognized in the ammonic sulphydrate precipitate, since in the presence of NH_5O and tartaric acid they behave like the phosphates. Treat the precipitate produced in one part by NH_5O in the presence of tartaric acid, with concentrated H_2SO_4, and when the HF has thereby been driven off, moisten the whole precipitate with H_2SO_4 and test the residue for phosphoric acid and Ba, Sr, Ca, Mg. The borates of the metals of the alkaline earths may be in the ammonic sulphydrate precipitate; boric acid is tested for in a part of the precipitate.

The filtrate from the ammonic sulphydrate precipitate is acidulated with HCl, heated to expel the H_2S, filtered from the separated sulphur, and the filtrate is tested for the metals of the alkaline earths and alkalis as previously directed.*

(D). METALS OF THE HYDROSULPHURIC ACID GROUP, WHOSE SULPHIDES ARE INSOLUBLE IN NH_5S.

15. MERCURY.

$Hg = 200$; $\dot{H}hg$† $= 400$.

This metal is silver-white; it is distinguished from all other metals by its fluidity. Melting point —40°, boiling point 360°, sp. gr. 13.5. In the air at ordinary temperatures it is unchanged; at a higher temperature it is oxidized to red HgO, which by ignition separates into Hg and O. HCl does not dissolve this metal. Dilute HNO_3, in presence of excess of mercury, dissolves the metal, forming $Hg_2N_2O_6$. If HNO_3 is in excess HgN_2O_6 is formed, particularly on heating.

Aqua regia dissolves the metal to $HgCl_2$.

a. Mercurous compounds.

Hg_2O is black; it forms no hydrate. The neutral salts are colorless. Some basic ones are yellow (*e. g.*, $Hhg_2N_2O_7$). From their solutions *caustic alkalies* precipitate black Hg_2O. NH_5O precipitates black amide compounds, *e. g.*, $Hg_2H_2N{\cdot}NO_3$. H_2S

* Exercise in analysis. Quantitative analysis of Augite or Hornblende.

† For convenience written Hg_2.

and NH_5S precipitate black Hg_2S, which is not soluble in HNO_3, but dissolves easily in aqua regia, forming $HgCl_2$.

Hydrochloric acid and *soluble chlorides* precipitate white Hg_2Cl_2; KI separates out greenish-yellow Hg_2I_2; KCy precipitates metallic Hg (formation of $HgCy_2$). $SnCl_2$ produces in solutions of mercuric salts, first a white precipitate of Hg_2Cl_2, which by excess of $SnCl_2$ becomes quickly gray by separation of Hg and formation of $SnCl_4$. *Sulphurous acid* also throws down metallic mercury.

b. Mercuric compounds.

HgO is red when produced by heating metallic Hg, yellow when it is formed by precipitation; mercuric oxide also forms no hydrate. The salts are colorless; they are decomposed in solutions with separation of basic salts (*e. g.*, $3\,HgSO_4 + 2\,H_2O = Hg_3SO_6 + 2H_2SO_4$). $HgCl_2$ and $HgCy_2$ do not have this property. From a solution of $HgCl_2$, NaHO throws down a yellow oxide; NH_5O produces in the fluid a white precipitate ("white precipitate" HgH_2NCl); KI throws down red HgI_2, which is soluble in excess of KI. H_2S and NH_5S produce in a solution of $HgCl_2$ first a white precipitate ($HgCl_2 + 2\,HgS$), which in excess of H_2S or NH_5S is black (HgS). This mercuric sulphide is insoluble in HNO_3, but is easily soluble in aqua regia. $SnCl_2$ and H_2SO_3 give first Hg_2Cl_2, then Hg.

From all mercury compounds copper separates out metallic mercury. All mercury salts give, when mixed with Na_2CO_3 and heated in a tube, a gray sublimate of metallic mercury.

SYNOPSIS.

	$Hg_2N_2O_6$	$HgCl_2$
HCl..................	Hg_2Cl_2	—
KI.....................	Greenish-yellow	Red
NaHO................	Black	Yellow
NH_5O................	Black	White
KCy....................	Hg_2	—

16. Lead.

$Pb = 207$.

This metal is gray, very soft, very malleable. Melting point 325°, sp. gr. 11.4. It is oxidized at ordinary temperatures only in moist air to PbH_2O_2, which quickly takes up CO_2. HCl does not dissolve the metal. H_2SO_4 dissolves the metal only when it is concentrated and heated. HNO_3 easily dissolves the metal to PbN_2O_6.

PbO is yellow; the hydrate PbH_2O_2 is white, slightly soluble in water (alkaline solution). The salts are mostly colorless. Caustic alkalis and NH_5O precipitate PbH_2O_2, soluble in KHO and NaHO. $PbCO_3$ is insoluble in water but easily soluble in caustic alkalis. H_2S and NH_5S throw down black PbS, which by heating in HNO_3 passes over into white insoluble $PbSO_4$. H_2SO_4 and *soluble sulphates* separate out $PbSO_4$, somewhat soluble in water, more difficultly soluble in water contain-

ing H_2SO_4, insoluble in alcohol, soluble in NaHO, in an ammoniacal solution of tartaric acid and in $Na_2S_2O_3$. HCl and *metallic chlorides* precipitate $PbCl_2$, soluble in much hot water.

All lead compounds give, when heated with KCy, or Na_2CO_3, heated on charcoal before the blowpipe, a malleable globule; the coal is covered with a yellow incrustation.

17. Silver.

Ag = 108.

This metal is white; sp. gr. 10.5, melting point about 900°. It is not oxidized at any temperature in the air, but when in the melted condition takes up oxygen, which it gives off on cooling. Its solvent is HNO_3.

Ag_2O is grayish brown, becomes black in the light (Ag_4O), is somewhat soluble in water, and gives an alkaline reaction; the hydrate is not known in the isolated state. The salts are mostly colorless and they are affected by light (reduction to Ag). *Caustic alkalis* precipitate Ag_2O insoluble in an excess; NH_5O throws down also Ag_2O, but this precipitate is easily soluble ($(NH_3)_2Ag_2O$); from acid solutions NH_5O precipitates nothing.

H_2S separates out black Ag_2S, soluble in HNO_3. HCl, HBr, HI, HCy, as well as their corresponding alkali compounds, precipitate AgCl, AgBr, AgI, AgCy. Only AgCy is soluble in concentrated HNO_3; AgI is alone insoluble in NH_5O; AgCy is alone decomposed on ignition. All these compounds are

soluble in KCy ($AgKCy_2$) and $Na_2S_2O_3$ ($Ag_2S_2O_3+2Na_2S_2O_3$). AgCl and AgBr are affected by light, becoming black with formation of Ag_2Cl etc. AgI is affected by light only in presence of bodies which can easily separate out I_2, *e. g.*, $AgNO_3$. Cu, Fe, Zn, H_2SO_3 and $FeSO_4$ precipitate metallic silver from solutions.

All silver compounds give, with KCy or Na_2CO_3, on charcoal before the blowpipe, a malleable globule without any incrustation.

SYNOPSIS.

	Hg_2Cl_2	$PbCl_2$	AgCl
H_2O ..	—	Soluble on heating	—
NH_5O.	Black.	Yellow when warm	Dissolves without color

18. Bismuth.

Bi = 210.

Bismuth is reddish-white, very brittle, has a melting point of 260°, a sp. gr. 9.8. It first oxidizes at a red heat in the air, and then burns with a blue flame. Its solvent is HNO_3. Of the three oxides Bi_2O, Bi_2O_3 and Bi_2O_5, only the middle one is treated of. Bismuth oxide is yellow, melts by heating, but is scarcely volatile. The hydrate (BiH_3O_3) is white. The salts are stable only in acid solutions; the neutral salts are decomposed by water with separation of basic salts (*e. g.*, $BiN_3O_9+H_2O=BiNO_4+$

$2HNO_3$; $3BiCl_3+3H_2O=Bi_2O_3\cdot BiCl_3+6HCl$). Acids again dissolve these basic salts, but tartaric acid does not hinder the separation of the basic compounds. NaHO and NH_5O throw down a white hydrate insoluble in excess of the precipitant. H_2S throws down black Bi_2S_3, soluble in HNO_3. KI separates out BiI_3 as a brown precipitate.

All bismuth compounds give on charcoal before the blowpipe, a brittle globule and a yellow incrustation.

19. Copper.

$Cu=63.4$; Ccu * $=126.8$.

The metal is red and ductile; its melting point is 1200°; sp. gr. 8.9. In moist air it is oxidized and forms a substance containing CuO_2 and CuH_2O_2; at a higher temperature it forms black CuO. HCl at ordinary temperatures acts upon it slightly with evolution of gas; at higher temperatures, or in the presence of oxygen, it dissolves it. H_2SO_4 only dissolves it when heated. HNO_3 dissolves the metal easily. Copper yields two basic oxides, CuO and Cu_2O, and their salts are distinguished as cupric and cuprous.

a. *Cuprous salts* (cuprous oxide compounds). Cu_2O is red; its hydrate, $Cu_2H_2O_2$, is yellow. The salts are colorless; NaHO precipitates yellow hydrate, which on heating passes over into anhydrous Cu_2O. NH_5O yields no precipitate ($(NH_3)_2Cu_2O$); the colorless ammoniacal solution becomes a deep

* Ccu is here written Cu_2.

blue on exposure to the air. (Cupramine) KCl, KI, KCy, KCyS and K_4FeCy_6 throw down white precipitates of Cu_2 salts; H_2S and NH_5S, black CuS.

Cupric salts (cupric oxide compounds). CuO is black; its hydrate is blue; the anhydrous salts are colorless; the hydrous blue. NaHO precipitates from solutions blue CuH_2O_2, which becomes black on heating, (CuO). NH_5O dissolves the precipitate, which at first appears with deep blue coloration $((NH_3)_2CuO)$. $(NH_4)_2CO_3$ behaves in like manner. H_2S precipitates CuS. KI throws down from cupric salts white Cu_2I_2 (liberation of I_2) this precipitation is aided by the presence of H_2SO_3. KCy and KCyS behave in the same way. Cu_2Cy_2 is soluble in excess of KCy $(Cu_2K_2Cy_4)$. From the colorless solution Cu_2Cy_2 is again precipitated by HCl. H_2S precipitates the copper from this solution only after a very long time. K_4FeCy_6 gives a reddish brown precipitate of $K_2Cu_3Fe_2Cy_{12}$. Tartaric acid prevents the precipitation of CuH_2O_2 by caustic alkalis. From such alkaline solutions containing tartaric acid, Cu_2O is separated on boiling with grape sugar.

Zn and Fe remove Cu from its solutions. All copper compounds color beads green in the oxidizing flame; in the reducing flame they become dark brown (opaque). All copper compounds yield a red ductile globule, before the blowpipe on charcoal, with Na_2CO_3 or KCy.

20. Cadmium.

$Cd=112$.

This metal resembles zinc and copper. It is white, malleable, volatilizes at 400°; sp. gr. 8.6. It dissolves easily in acids.

CdO is brown, unchanged by heat; its hydrate is white. The salts are colorless. $NaHO$ separates out from solutions of these salts white CdH_2O_2 insoluble in excess of $NaHO$. NH_5O easily redissolves the corresponding precipitate of CdH_2O_2. Acid solutions are not precipitated by NH_5O. $(NH_4)_2CO_3$ does not redissolve the cadmium carbonate which it throws down. H_2S and NH_5S give yellow CdS. KCy precipitates white $CdCy_2$, soluble in excess; from this solution H_2S throws down all the Cd.

All cadmium compounds give upon charcoal before the blowpipe a dark brown incrustation (without a metalic globule).

Analysis of the Hydrosulphuric Acid precipitate insoluble in NH_5S.

From the slightly acid solution through which H_2S as a gas has been passed to complete saturation of the liquid, HgS, PbS, Ag_2S, Bi_2S_3, CuS and CdS are thrown down.

The precipitate is collected upon a filter, washed with water and then heated in a capsule with concentrated HNO_3 (free from HCl).

1. *Residue.* HgS and $PbSO_4$. The residue separated from the solution is digested with an

ammoniacal solution of tartaric acid. $PbSO_4$ is thus dissolved, the solution is filtered from some undissolved residue which may remain, and in the filtrate the lead is recognized by means of H_2S. The portion undissolved by the ammoniacal tartaric acid solution is dissolved in aqua regia, the excess of acid driven off by evaporation, and finally the solution is tested with $SnCl_2$ for mercury.

2. *Solution.* In order to thrown down any dissolved lead the solution is treated with a little H_2SO_4. The filtrate from the precipitate thus formed is tested by HCl for silver, then filtered again, and from the solution bismuth is thrown down by NH_5O. If the filtrate from the bismuth hydrate is blue, copper is indicated. To detect copper in the presence of cadmium, decompose the ammoniacal solution by means of KCy until it becomes colorless, then H_2S will precipitate yellow CdS.*

(E). METALS OF THE HYDROSULPHURIC ACID GROUP, WHOSE SULPHIDES ARE SOLUBLE IN NH_5S.

21. TIN.

$Sn=116$.

Tin is silver-white; very malleable. Melting point 230°, sp. gr. 7.29. It oxidizes at a high temperature in the air. HCl and H_2SO_4 dissolve the metal with evolution of H_2. HNO_3 diluted and used in the cold, dissolves tin with formation

* Exercise for practice. Quantitative analysis of copper ore, silver-coin, silver ore, brass.

of $NH_4, \cdot NO_3 (4\,Sn + 10\,HNO_3 = 4\,SnN_2O_6 + NH_4 \cdot NO_3 + 3\,H_2O)$; when heated there is formed an insoluble SnO_2 with evolution of NO. Aqua regia dissolves tin to $SnCl_4$; KHO dissolves it to K_2SnO_3.

a. *Stannous compounds* (protoxide salts). SnO is dark gray, the hydrate is white. SnO oxidizes in the air at a red heat to SnO_2 (white). Stannous salts are colorless, oxidizable especially in solutions exposed to the air, forming stannic salts and separating out SnO_2. They act as powerful reducing agents, (Fe_2Cl_6 becomes, by action of $SnCl_2$, $FeCl_2$; Hg_2Cl_2 becomes 2 Hg.) From their solutions NaHO, Na_2CO_3 and NH_5O precipitate white SnH_2O_2 soluble in excess of NaHO, from which solution by heating it is thrown down as black SnO.

H_2S separates out dark brown SnS, which dissolves in yellow ammonic sulphydrate (oxidizing in the air thereby forming polysulphides). From this solution HCl precipitates yellow SnS_2. HCl_2 gives in a solution of $SnCl_2$ a white precipitate of Hg_2Cl_2, from which, in excess of $SnCl_2$, metallic mercury separates. $AuCl_3$ gives in solutions of stannous salts which by standing in the air have become oxidized and hence contain also stannic salts, a precipitate of gold-purple (Purple of Cassius) ($2\,AuCl_3 + 2\,SnCl_2 + SnCl_4 + 11\,H_2O = (Au_2Sn_3O_7 + 4H_2O) + 14\,HCl$).

b. *Stannic compounds.* SnO_2 is white, becoming yellow when heated. HCl throws down from a solution of SnO_2 in KHO stannic oxide which is soluble in an excess of HCl; HNO_3 oxidizes the metal to SnO_2 (metastannic acid), soluble in HCl when

heated and afterward diluted with water. $SnCl_4$ is a fluid. $NaHO$, NH_5O and Na_2CO_3 precipitate SnO_2 soluble in $NaHO$. H_2S throws down yellow SnS_2 soluble in NH_5S ($SnS_2 + 2\,NH_5S = (NH_4)_2SnS_3 + H_2S$) and in $NaHO$($3\,SnS_3 + 6\,NaHO = 2\,Na_2SnS_3 + Na_2SnO_3 + 3\,H_2O$), insoluble in $(NH_4)_2CO_3$.

From all solutions of tin, zinc separates out metallic tin. All tin compounds give on charcoal before the blowpipe a malleable globule; near the assay there is a slight white incrustation.*

SYNOPSIS.

	$SnCl_2$	$SnCl_4$
H_2S	Brown.	Yellow
$HgCl_2$	Hg_2Cl_2—Hg.	—
$Fe_2Cl_6 + K_6Fe_2Cy_{12}$	Blue.	—

22. Arsenic.

At. $As = 75$; Mol. $As_4 = 300$.

A steel-gray crystalline brittle mass, having a specific gravity of 5.96. It is volatilized on heating without melting. The vapor has a specific gravity of 10.4. It gradually oxidizes in moist air to AS_2O_3. Heated to redness in a current of air it burns to As_2O_3, emitting an odor of garlic. Arsenic is insoluble in HCl and H_2SO_4, but dissolves in HNO_3

* Analysis of an alloy of lead and tin, for instance, soft solder. Analysis of bronze.

with formation of As_2O_3; or if the acid be concentrated, of As_2O_5.

a. *Arsenious acid.* As_2O_3, hydrate $H_2As_2O_4$, is a vitreous mass which soon becomes opaque by the formation of the crystalline modification. Arsenious acid is volatile; the vapor is odorless, and deposits a sublimate of white octahedral crystals in the colder part of the matrass. It dissolves with difficulty in water (50 parts of cold, and 10 parts of boiling water dissolve 1 part of As_2O_3), easily dissolves in HCl and HNO_3 (formation of As_2O_5) and in alkaline fluids. Only the arsenites of the alkalis are soluble in water; all are decomposed at a red heat, either into oxide and arsenous acid ($CaAs_2O_4$) or into arsenic and arsenate ($Na_2As_2O_4$). H_2S separates yellow As_2S_3 (gradually) soluble in NH_5S, KHO, $(NH_4)_2CO_3$, and $KHSO_3$($2\,As_2S_3 + 4\,(NH_4)CO_3 = (NH_4)_2As_2O_4 + (NH_4)_6As_2S_6 + 4\,CO_2$; $2As_2S_3 + 16\,KHSO_3 = 2\,K_2As_2O_4 + 6\,K_2S_2O_3 + 3\,S + 7\,SO_2 + 8\,H_2O$. From the solution in NH_5S, KHO or $(NH_4)_2CO_3$, all the arsenic is precipitated again as As_2S_3 by HCl. If As_2O_3 is fused with Na_2CO_3 and $NaNO_3$, a soluble arsenate is produced. Argentic arsenite is of a characteristic yellow color ($Ag_2As_2O_4$). This is soluble in NH_5O and in HNO_3. If As_2O_3 be sublimed on the wall of a capsule, the sublimate moistened with $AgNO_3$ and a little NH_5O be now added, to neutralize the free HNO_3, there appears distinctly a yellow color.

As_2O_3 acts as a reducing agent, (CrO_3 becomes Cr_2O_3, CuO, in alkaline solutions containing tartaric acid becomes Cu_2O).

b. *Arsenic acid.* As_2O_5; hydrated H_3AsO_4 (analogous to H_3PO_4) forms clear large crystals, when melted it gives off water, and leaves behind a vitreous mass As_2O_5. It is easily soluble in water; the alkaline arsenates only are soluble in water. Of the insoluble there are characteristic Ag_3AsO_4, a brownish red precipitate soluble in NH_5O and HNO_3; and $MgNH_4AsO_4$ which behaves like the corresponding phosphate but is decomposed at a low red heat.

H_2S throws down $As_2S_3 + 2\,S$. The necessary deoxidation of As_2O_5 to As_2O_3 proceeds very slowly in the cold; the fluid is, therefore, heated to about 50° and then saturated with H_2S.

SYNOPSIS.

	As_2O_3	As_2O_5
$AgNO_3(NH_5O)$	Yellow	Brownish-red
K_2CrO_4	Green	—
Alkaline solution of CuO..	Cu_2O	—
$MgSO_4(NH_4Cl)$............	—	$MgNH_4AsO_4$

c. *Arsenetted hydrogen,* AsH_3. If a sulphuric acid solution of the salts of arsenious or arsenic acid, placed in an apparatus in which H_2 is evolved by the action of dilute H_2SO_4 upon zinc, all the arsenic will be driven off as AsH_3 (As_2S_3 or As_4 do not give off this gas, free Cl_2, HNO_3 and other oxidizing substances also hinder the production of AsH_3).

This gas is colorless, possesses an odor of garlic, and acts as a powerful poison.

By complete combustion it becomes H_2O and As_2O_3, by imperfect combustion H_2O and As_4. From AsH_3 the arsenic can be separated as a mirror or as an arsenic stain; the gas can be recognized also by passing it into a solution of $AgNO_3$.

The mirror is formed when AsH_3 is passed through a red-hot glass tube; the As_4 separates behind the heated portion of the tube in a thin opaque layer as a mirror of brown color. The mirror is easily volatilized in the tube, volatilizing even before melting.

Arsenic stain is obtained when the stream of gas issuing from Marsh's apparatus is lighted and a porcelain capsule held in the flame. The porcelain glazing must be free from lead. These stains are also brownish black, brightly glimmering and brown on the edges. They dissolve in NaClO; give, when treated with NH_5S and dried, a yellow residue of Ag_2S_3, and yield with $AgNO_3$ and NH_5O, when oxidized by HNO_3, a yellow $Ag_2As_2O_4$. When AsH_3 is conducted into *a slightly acid solution* of $AgNO_3$, Ag is precipitated and there remains in solution $Ag_2As_2O_4$($2\,AsH_3 + 14\,AgNO_3 + 4\,H_2O = Ag_2As_2O_4 + 12\,Ag + 14\,HNO_3$). After filtration from the Ag and neutralization by NH_5O the characteristic yellow silver precipitate is formed. In order to recognize the arsenic acid compounds, in the dry way, the substance is placed in the bottom of a narrow matrass, heated and when the vapor has ceased to appear, a mirror will be formed in the colder part of the

tube. As_2S_3 is melted in a matrass with a mixture of KCy and Na_2CO_3, in this case also a mirror is formed. On charcoal before the blowpipe the arsenic compounds, when ignited, give off the characteristic garlic odor.*

23. ANTIMONY.

$Sb = 122$.

Sb is a tin-white, crystalline, very brittle body, of 6.7 sp. gr.; its melting point is 425, but it is volatile at a white heat. Heated to redness in a current of air it evolves vapors of Sb_2O_3. Concentrated HNO_3 oxidizes antimony, forming Sb_2O_4 ($Sb_2O_3 + Sb_2O_5$). Aqua regia dissolves it with formation of $SbCl_3$ or $SbCl_5$, according to the degree of concentration of the acids.

a. *Antimonous oxide* (antimonous acid), Sb_2O_3, forms brilliant needles, which cover the surface of antimony when it is incompletely consumed. It melts at a high temperature; thus heated it is volatile in a current of air; at a red heat it yields with free access of air, Sb_2O_4. Sb_2O_3 is insoluble in water, but it easily dissolves in HCl, acetic acid and KHO. The solution in hydrochloric acid becomes turbid on addition of water by the precipitation of a basic salt ($5\,Sb_2O_3 \cdot 2\,SbCl_3$).

In much hydrochloric acid the precipitate is dissolved; tartaric acid prevents the precipitation by water (distinction from bismuth). From the hydro-

* Quantitative estimation of Cu and As in Schweinfurt green.

chloric acid solution of antimonous oxide, H_2S precipitates orange-red Sb_2S_3, which is soluble in concentrated HCl, in KHO, NH_5O, but only very slightly in $(NH_4)_2CO_3$. With Na_2CO_3 and $NaNO_3$ antimonous sulphide yields, when fused, $NaSbO_3$, insoluble in water. The hydrochloric acid solution of antimonous oxide precipitates metallic gold from its solution ($2\,AuCl_3 + 3\,SbCl_3 = 2\,Au + 3\,SbCl_5$). Metal zinc precipitates from such a solution antimony as a black powder, especially in platinum vessels.

b. *Antimonic acid*, Sb_2O_5, is a white mass which is formed by treating antimony with an excess of concentrated HNO_3. It is slightly soluble in water, but dissolves readily in KHO ($KSbO_3$) and in HCl ($SbCl_5$). This HCl solution is decomposed by water ($2\,SbCl_5 + 5\,H_2O = 10\,HCl + Sb_2O_5$). Tartaric acid prevents this decomposition. H_2S precipitates from acid solutions of antimonic acid red Sb_2S_5. The precipitate is soluble in NH_5S and in KHO ($4\,Sb_2S_5 + 18\,KHO = 5\,K_3SbS_4 + 3\,KSbO_3 + 9\,H_2O$). From this solution the Sb_2S_5 is again precipitated by HCl. Concentrated HCl dissolves the Sb_2S_5 to $SbCl_3$.

The solution of Sb_2O_5 in KHO gives with sodium salts a white precipitate of $Na_2H_2Sb_2O_7$. Solutions of antimonic acid precipitate from auric chloride no metallic gold.

c. *Antimonetted hydrogen*, SbH_3, produced like AsH_3, is very much like it. They differ in the following particulars, SbH_3 is odorless, the gas conducted over solid KHO is decomposed with formation of SbK_3 ($SbH_3 + 3\,KHO = SbK_3 + 3\,H_2O$). By incomplete combustion, and by conducting it through a red hot

tube there are obtained the antimony stain and mirror. These are entirely opaque; in a thin layer they appear as a spot on the glass or porcelain; in a thicker layer they are quite black or possess a lustre like graphite. They volatilize on heating before melting; they are insoluble in NaClO; they are changed by NH_5S into orange red Sb_2S_3. If the stain is oxidized with HNO_3 it yields a white residue of Sb_2O_4 on evaporating; moistened with $AgNO_3$ and then treated with NH_5O, a *black* stain is produced ($Sb_2O_4 + 4\,AgNO_3 + 2\,H_2O = Sb_2O_5 + Ag_4O + 4\,HNO_3$). When SbH_3 is conducted into a solution of $AgNO_3$, Sb and Ag are thrown down, the filtrate from this precipitate contains no antimony ($2\,SbH_3 + 6\,AgNO_3 = 2\,Sb + 6\,Ag + 6\,HNO_3$).

On charcoal before the blowpipe, the antimony compounds mixed with KCy and ignited, give a little brittle metallic globule, while the coal is covered with a white incrustation which is volatile before the blowpipe flame. When antimony compounds are ignited upon an asbestos support, in an oxidizing flame, there is deposited on a porcelain capsule held over the flame, a sublimate of Sb_2O_4, which can be identified by $AgNO_3$ and NH_5O.*

Detection of Arsenic, Tin and Antimony in the presence of each other.

The precipitate obtained from the weak acid solution of the original substance by completely saturating the liquid with H_2S, is collected on a

* Analysis of type metal and gray silver ore.

filter and washed with water which contains H_2S. The filter is then perforated, the precipitate washed down with water containing NH_5S, into a flask; in this some more NH_5S is placed and the mass gently heated in the flask. The insoluble portion is collected on a filter and treated after the requisite washing, as directed on page 68. The filtrate is acidified with H_2SO_4 by which As_2S_3, Sb_2S_3 and SnS_2 are precipitated. (If the precipitate resulting from this is of a dark color, it may contain Au, Pt, Mo, Wo, etc). In order to detect the three compounds one of the following methods is employed.

1. The precipitate is placed in a porcelain capsule, oxidized with fuming nitric acid and evaporated to dryness on the water bath. The yellow residue is taken up with a few drops of NaHO, the solution is mixed with Na_2CO_3 and $NaNO_3$, the resulting solidified mass is placed in a porcelain crucible, carefully dried, then fused and the fused mass after cooling is extracted with water. This solution contains Na_3AsO_4; $NaSbO_3$ and SnO_2 remain undissolved. Traces of SnO_2 might pass into solution. The solution is therefore heated with sodium bi-carbonate when As entirely dissolves. Sb and Sn remain undissolved.

2. The precipitate is placed in a flask, digested with $(NH_4)_2CO_3$ and filtered. Sb_2S_3 and SnS_2 are not dissolved, but As_2S_3 can be precipitated from the filtrate by HCl. Slight traces of tin are dissolved with the arsenic.

The precipitate is dissolved in KHS, the solution is mixed with a large excess of aqueous sulphurous

acid, heated until SO_2 ceases to come off, and filtered. Only As_2S_3 is in solution, Sb_2S_3 and SnS_2 are undissolved, As_2S_3 is precipitated from the filtrate by H_2S.

A. *Detection of Arsenic.*

The solution 1 of the arseniates is heated with H_2SO_4 until all the HNO_3 is driven off, but the precipitate of As_2S_3 which was obtained in 2 and 3 is dissolved in excess of HCl and a little $KClO_3$, the solution is evaporated and the residue heated with sulphuric acid.

The sulphuric acid solution is placed in a Marsh apparatus, and the As is thereby indicated.

B. *Detection of Tin and Antimony.*

The mixture of tin and antimony compounds which exists in any case is heated upon the filter in a crucible until the paper is consumed, solid potassic cyanide added and carefully heated to fusion. Antimony and tin will be reduced. The mass is extracted with water and the insoluble metallic residue treated with HCl. Only the tin is dissolved, and this may be recognized by HCl_2. If HCl dissolves nothing, aqua regia is used, the excess of acid driven off by heat, and a part of this solution tested with H_2S for antimony. Another part is placed in a Marsh apparatus to obtain the antimony mirror and stain. Or the mixture is dissolved in concentrated HCl, evaporated upon the water bath, diluted largely with water, the metals precipitated by a zinc rod and the precipitated metals tested as previously directed.

APPENDIX

TO

LABORATORY GUIDE.

DETECTION OF CERTAIN ORGANIC SUBSTANCES.

1. Cyanogen Compounds.

Cyanogen, $C_2N_2 = Cy_2$, is a colorless gas; it is offensive to the nose and eyes. It burns with a violet bluish-bordered flame; is soluble in water, alcohol and ether. The aqueous solution is quickly decomposed with formation of prussic acid, ammonic oxalate, ammonic carbonate and urea. Cyanogen resembles a monatomic metalloid in its reaction; it has the greatest similarity to chlorine ($Cy_2 + 2\,KHO = KCy + KCyO + H_2O$).

Hydrocyanic acid, HCy (prussic acid) is an extremely volatile liquid (boiling point 26.5°), which possesses an odor resembling that of bitter almonds, and is very poisonous. It easily dissolves in water; this solution is decomposed with formation of ammonic formiate ($HCN + 2\,H_2O = CH.NH_4.O_2$). The compounds of cyanogen with the metals of the alkalis and of the alkaline earths are soluble in water ($HgCy_2$ dissolves also); all others are insoluble in water, but easily dissolve in KCy with formation of

double salts. All metallic cyanides (except KCy and NaCy) are decomposed at a red heat; by exclusion of air they yield cyanogen, by its access they form cyanates. All cyanogen compounds, heated with HCl, yield HCy. With concentrated H_2SO_4, they yield CO ($KCN + 2\,H_2SO_4 + H_2O = KHSO_4 + NH_4HSO_4 + CO$). Soluble metallic cyanides, with $AgNO_3$, give a white, curdy precipitate, AgCy, which is soluble in NH_5O; is not dissolved by dilute HNO_3, but in concentrated HNO_3, in KCy, $Na_2S_2O_3$ can easily be dissolved. AgCy with HCl yields prussic acid; is decomposed at a red heat. From $CuSO_4$, on addition of KCy, white Cu_2Cy_2 precipitate, which combines with KCy to form a colorless compound. $FeSO_4$ first gives, with KCy, $FeCy_2$, which, in excess of KCy, especially in the presence of KHO, is dissolved with formation of K_4FeCy_6. If now Fe_2Cl_6 be added, there is formed Prussian blue ($Fe_4Fe_3Cy_{18}$). In order to prove the presence of cyanogen, the solution to be tested is mixed with some $FeSO_4$, to which a little Fe_2Cl_6 is added, supersaturated with NaHO, and then rendered acid with HCl; a blue precipitate insoluble in HCl indicates cyanogen. From Fe_2Cl_6, KCy precipitates $Fe_2H_6O_6$. Heated with yellow ammonic sulphide the cyanogen compounds yield combinations of sulphur and cyanogen, which, after driving off the excess of NH_5S, with Fe_2Cl_6, give a blood red color, which does not disappear on adding HCl. Heated with KHO, the metallic cyanides evolve NH_3. The insoluble double cyanides are decomposed by boiling with HCl, the distillate is collected in NaHO, and then this is tested for NaCy.

Potassic ferrocyanide, K_4FeCy_6, gives with $FeSO_4$, a white precipitate ($Fe_2K_2Cy_6$); with Fe_2Cl_6, Prussian blue ($Fe_4Fe_3Cy_{18}$); with $CuSO_4$, a brown red precipitate ($K_2Cu_3Fe_2Cy_{12}$).

Potassic ferridcyanide yields with $FeSO_4$ a blue precipitate ($Fe_3Fe_2Cy_{12}$).

Prussian blue always yields Na_4FeCy_6 and $Fe_2H_6O_6$ on boiling with NaHO.

Cyanates (*e. g.*, KCyO) easily decompose, taking up water, into CO_2 and NH_3 ($HCNO + H_2O = CO_2 + NH_3$). With alkalis they evolve NH_3; with acids CO_2, which always contains traces of HCyO, and on this account smells offensively.

Sulphocyanates (KCyS) give with Fe_2Cl_6 a blood red color.

In the presence of cyanogen it is often difficult to recognize the metals by their ordinary reactions. If cyanogen has been detected, it is best to decompose the salts by evaporation with concentrated H_2SO_4; the residue then consists of sulphates.

In order to recognize cyanogen, chlorine, bromine and iodine in the presence of each other, they are all precipitated by $AgNO_3$. One portion of the precipitate is tested with HCl for AgCy; the remainder is heated to redness in order to destroy the AgCy. The residue, after heating, is treated with Zn and dilute H_2SO_4; Ag will separate; $ZnSO_4$ at the same time passes into solution together with HCl, HBr, and HI. This solution is neutralized with Na_2CO_3, boiled, filtered from $ZnCO_3$, and now there remains a liquid in which NaCl, NaBr, NaI, will be easily recognized as formerly pointed out.

2. Organic Acids.

Most organic acids and their compounds are decomposed by heating on charcoal. At the same time, if the acid is in union with metals of the alkalis or of the alkaline earths, carbonates are formed. The blackening of a substance at a red heat and the formation of carbonates are means of recognition of the presence of organic acids. Oxalic acid and its salts do not blacken at a red heat.

a. *Oxalic acid*, $C_2H_2O_4$, is a dibasic acid. It is decomposed by heat, either by itself or with H_2SO_4 into H_2O, CO_2, and CO. The last burns with a blue flame. Oxalic acid and soluble oxalates give with soluble calcic compounds a white precipitate, CaC_2O_4. Calcic oxalate is insoluble in ammonic salts and acetic acid, but is easily soluble in HCl. From this solution the precipitate will again be thrown down by means of $C_2H_3NaO_2$.

b. *Tartaric acid*, $C_4H_6O_6$, is dibasic. It gives out a characteristic odor on burning. The neutral solution of a tartrate gives with $CaCl_2$ a precipitate $C_4H_4CaO_6$. This precipitate is more soluble in water than gypsum; a solution of $CaSO_4$, therefore, does not affect it. The precipitate does not occur in very dilute solution. Calcic tartrate is soluble in acids, even in free tartaric and acetic acids; it is soluble in ammonic chloride (NH_4Cl) and in caustic alkalis. Free tartaric acid, or a concentrated solution of a tartrate, acidified with acetic acid, gives with KCl a crystalline precipitate, $C_4H_5KO_6$, especially if the sides of the tube be rubbed with a glass rod. Cream

of tartar is soluble in strong acids and in alkaline fluids.

c. *Citric acid*, $C_6H_8O_7$, is tribasic. Neutral solutions of a salt of citric acid give no precipitate with $CaCl_2$ in the cold; but if some NH_5O be added and the solution be heated to boiling, the salt $Ca_3(C_6H_5O_7)_2$ precipitates; it is soluble in acids.

d. *Malic acid*, $C_4H_6O_5$ is dibasic. The neutral or ammoniacal solution of a malate is not decomposed either cold or at a boiling temperature by $CaCl_2$. But alcohol precipitates calcium malate. If a neutral solution of a malate be mixed with $C_4H_4PbO_4$, a precipitate of $C_4H_4PbO_5$ occurs. If this precipitate be collected on a filter, washed, placed in water and heated, it becomes a transparent resinous mass.

To recognize the four acids in the presence of each other.

The neutral concentrated solution of the substance (best prepared by boiling the original substance with Na_2CO_3, filtering and neutralizing the filtrate with HNO_3) is decomposed by $CaCl_2$.

1. *Precipitate.* C_2CaO_4 and $C_4H_4CaO_6$. It is to be washed with water, then dissolved in HCl and the solution treated with $C_2H_3NaO_2$. C_2CaO_4 precipitates. Filter and test the acetic acid filtrate with KCl for tartaric acid.

2. *Filtrate.* This is made slightly alkaline with NH_5O and boiled. By this means $Ca_3(C_6H_5O_7)_2$ separates. Filter, precipitate calcium malate from the filtrate with alcohol; collect this on a filter, wash with alcohol and dissolve in water; determine the

presence of malic acid by means of the characteristic reaction of plumbic salts.

If in the neutral solution oxalic and tartaric acids are present, together with phosphoric acid, all three acids will go down with $CaCl_2$. In order, then, to find the three acids, the precipitate is dissolved in HCl; calcium oxalate, only, is thrown down by means of $C_2H_3NaO_2$, and removed by filtration. $CaHPO_4$ will only separate from the acetic acid solution by means of NH_5O and NH_4Cl. This is to be collected on a filter, and finally the filtrate, made slightly acid, is tested with KCl for tartaric.

e. *Acetic acid*, $C_2H_4O_2$, is monobasic. The acetates give the characteristic odor of acetic acid with H_2SO_4. If alcohol be added there is produced acetic ether, $C_2H_3(C_2H_5)O_2$, which is easily recognized by its odor. Neutral solutions of the acetates with $FeCl_6$ give a blood red color, which disappears on addition of HCl (different from sulphocyanates).

On boiling the blood red solution, all the iron separates as $Fe_2H_6O_6$, with a little acetic acid. A dry acetate, heated with some solid caustic potassa and As_2O_3, yields the most disagreeably smelling kakodyle.

f. *Formic acid*, CH_2O_2 is monobasic. The formiates are very similar in their deportment to the acetates; but they differ from them in their power to reduce many metals from their compounds. From silver and mercury salts they separate the metal, especially on heating. Formic acid with H_2SO_4 yields H_2O and CO.

g. *Tannic acid* and *gallic acid* ($C_7H_6O_5$) are eas-

ily recognized by the black precipitate which they produce with ferroso-ferric compounds. They differ from one another in this, that tannic acid is precipitated by solution of gelatin, and animal skins, but gallic acid is not.

h. *Succinic acid* ($C_4H_6O_4$) is dibasic; *Benzoic acid* ($C_7H_6O_2$), monobasic. Both, on being heated to redness by themselves or on warming their salts with H_2SO_4, volatilize in vapors which provoke vehement coughing. Both give in neutral solutions a brown red precipitate with Fe_2Cl_6.

Succinic acid in an ammoniacal solution with $BaCl_2$ gives a precipitate, but is not precipitated from the solutions of its salts in H_2SO_4 (is soluble in H_2O).

Benzoic acid forms a soluble barium salt; is precipitated from concentrated solutions of its salts, by acids (is soluble in H_2O with difficulty), and gives on heating with CaH_2O_2, benzol, recognized by its smell.

i. *Uric acid* ($C_5H_4N_4O_3$). It is nearly insoluble in water and dilute acids; soluble in alkalis, but is precipitated from such solution on addition of acids. If uric acid be oxidized with concentrated HNO_3 and the resulting solution evaporated to dryness on the water bath, and the residue moistened with NH_5O, it becomes purple red (murexid). Uric acid separates, from Ag_2CO_3, metallic silver, which is easily thrown on paper.

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